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THE GEOMETRY OF IMAGE FORMATION IN X-RAY ANALYSIS.

By Horace Scudder Uhler.

Introduction.—The theory of diffraction as applied to ordinary surface gratings and to the design of apparatus used in the spectroscopy of radiations having wave-lengths much greater than those of *X*-rays has been thoroughly worked out, and the most important results obtained are clearly presented in various places, for example, in Kayser's Handbuch der Spectroscopie. The theory of plane space-gratings (rigid crystals) has also been investigated by Laue and Bragg. On the other hand, as far as I have been able to ascertain, from a fairly complete search of the accessible literature of the subject, very little has been published on the general theory upon which the construction of *X*-ray spectrometers and spectrographs should be based. Accordingly, it may not be superfluous to present the results of my analytical study of some of the questions which arose both during the time when Dr. C. D. Cooksey and I were working on the high frequency spectrum of gallium and later when we were engaged in designing a new *X*-ray spectrograph for the accurate determination of the wave-lengths of characteristic radiations. Since these wave-lengths are too short to produce diffraction patterns of sensible dimensions, the problems fall within the domain of geometrical optics. As the interference and reflection methods used respectively by Laue and by Bragg lead, of necessity, to the same conclusions, and since the second point of view is the more advantageous for the present purposes, the crystals will be treated as aggregates of reflecting planes throughout the paper. The grating-space of the crystal, the wave-length of the rays, and the order of the spectrum will be considered as constants so that the glancing-angle γ will also be constant, conformably to the well-known relation $m\lambda = 2d \sin \gamma$.

General Equations.—Since a material space-lattice consists of a number

of parallel planes of regularly spaced atoms, a first approximation to the case of a real crystal may be made by studying the properties of a single plane of unlimited area which reflects rays of a given wave-length at a constant glancing-angle γ. Accordingly, the first question for consideration will be: To find the general equations of a ray reflected from a perfectly selective mirror when the position and direction of the incident ray are given in terms of certain convenient parameters.

Let the incident ray $\overline{SI}$ (Fig. 1) be determined by the point $S\ (x_1, y_1, z_1)$ and the angles α and β. α is the angle which the orthogonal projection of the incident ray on the plane XOY makes with the negative direction of the axis $\overline{OY}$. β is the angle which the ray $\overline{SI}$ forms with this projection. Hence, α and β may be looked upon as giving the azimuth and altitude of the incident ray, respectively. The mirror MO may rotate around $\overline{OZ}$ as axis. θ is the angle made by any normal to the mirror (such as $\overline{ON}$) with the coördinate plane XOZ. $I\ (x', y', z')$ denotes the point of incidence, and $\overline{IR}$ indicates the reflected ray. The equation of the reflector is

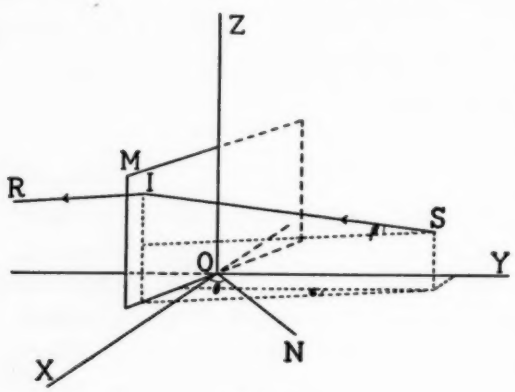

Fig. 1.

$$\cos\theta \cdot x + \sin\theta \cdot y = 0. \tag{1}$$

By spherical trigonometry (or otherwise) it is easy to show that the direction cosines of the incident ray are $\sin\alpha\cos\beta$, $-\cos\alpha\cos\beta$, and $\sin\beta$. Hence, the equations of this ray are

$$\frac{x - x_1}{\sin\alpha\cos\beta} = -\frac{y - y_1}{\cos\alpha\cos\beta} = \frac{z - z_1}{\sin\beta}. \tag{2}$$

From equations (1) and (2) the coördinates of the point of incidence I are found to be

$$\left.\begin{aligned} x' &= \frac{(x_1\cos\alpha + y_1\sin\alpha)\sin\theta}{\sin(\theta - \alpha)}, \\ y' &= -\frac{(x_1\cos\alpha + y_1\sin\alpha)\cos\theta}{\sin(\theta - \alpha)}, \\ z' &= z_1 + \frac{(x_1\cos\theta + y_1\sin\theta)\tan\beta}{\sin(\theta - \alpha).} \end{aligned}\right\} \tag{3}$$

Let l, m, and n denote the direction cosines of the reflected ray so that the equations of this line may be written

$$\frac{x - x'}{l} = \frac{y - y'}{m} = \frac{z - z'}{n}. \tag{4}$$

Since directions alone are now involved, expressions for l, m, and n in terms of α, β, and θ may be obtained by moving all necessary lines parallel to themselves until they radiate from the center of an auxiliary sphere.

In Fig. 2, $\overline{OI}$, $\overline{OR}$, and $\overline{ON}$ are parallel respectively to the incident

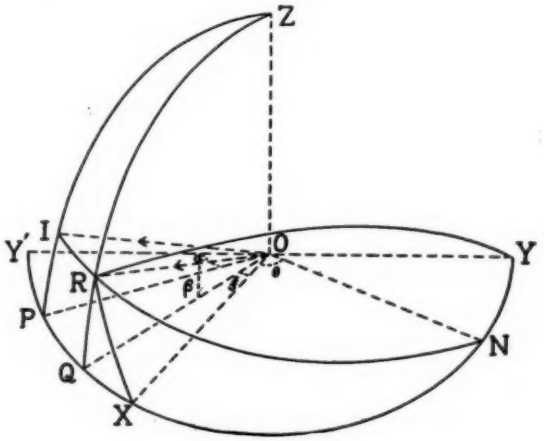

Fig. 2.

ray, the reflected ray, and the normal to the mirror. The law of reflection requires that $\angle QOR = \angle POI$ $(= \beta)$. Arcs of great circles are drawn through the various points as shown in the diagram. $\angle Y'OP = \alpha$, $\angle XON = \theta$. Let $\angle QOX \equiv \xi$. $\angle IOR = 2\gamma$ = deviation of ray.

In the rt. $\triangle QNR$,

$$\cos\left(\frac{\pi}{2} - \gamma\right) = \cos\beta\cos(\theta + \xi).$$

In the rt. $\triangle PNI$,

$$\cos\left(\frac{\pi}{2} + \gamma\right) = \cos\beta\cos\left(\theta + \frac{\pi}{2} - \alpha\right),$$

or

$$\sin\gamma = \cos\beta\sin(\theta - \alpha); \tag{5}$$

hence

$$\xi = \frac{\pi}{2} - (2\theta - \alpha).$$

In the rt. $\triangle QXR$,

$$l = \cos\beta \cos\xi$$

or

$$l = \cos\beta \sin(2\theta - \alpha); \tag{6}$$

In the rt. $\triangle QYR$,

$$m = \cos\beta \cos\left(\frac{\pi}{2} + \xi\right)$$

or

$$m = -\cos\beta \cos(2\theta - \alpha), \tag{7}$$

$$n = \sin\beta. \tag{8}$$

In general, being given α, β, and γ relation (5) furnishes two supplementary values for $\theta - \alpha$. Hence the values of θ corresponding to the two possible angular positions of the reflecting plane are determined. Having chosen the value of θ which is required, or which is compatible with the position of the point S (Fig. 1), l and m are given by formulæ (6) and (7), respectively. Since the coördinates x_1, y_1, and z_1 are also supposed to be known, the values of x', y', and z' may be computed at once from (3). Therefore the six parameters of equations (4) have been theoretically evaluated from the assigned data.

The preceding analysis is pertinent to the theory of the design of X-ray spectrometers in two respects: (*a*) it facilitates the actual calculation of the position and direction of the reflected ray so that its intersection with a photographic plate, or its path in an ionization chamber, can be predicted from the hypothetical positions of slits, diaphragms, etc.—in particular, spurious images and stray rays can be anticipated and eliminated; and (*b*) the numbered formulæ may be combined in various ways leading to conditional equations having useful interpretations. It may also be remarked that, as far as my information goes, all the papers which relate to the geometry of "image" formation with plane crystals restrict the problem to two dimensions, or more precisely, to pencils of rays lying in one plane perpendicular to the axis of rotation of the crystal ($\beta = 0$). Although these uniplanar problems are undoubtedly the simplest and most important, nevertheless they afford no information as to what happens when the angular altitude of the rays is not equal to zero. As will appear later, images may be widened unsymmetrically and appreciably, under special circumstances, due to the fact that β is not sufficiently small.

Complete Ray Determined by Two Points.—A solution of the following problem will now be outlined: To find a formula for θ being given the value of the glancing-angle γ and the two independent conditions that

the incident and reflected rays shall pass through the fixed points (x_1, y_1, z_1) and (x_2, y_2, z_2), respectively. Equations (4) already satisfy the first condition hence they will involve both conditions when written as

$$m(x_2 - x') = l(y_2 - y'),$$
$$n(x_2 - x') = l(z_2 - z').$$

Substitution, in the first equation, of the expressions for x', y', l, and m given by (3), (6), and (7) leads to

$$(x_1 \sin 2\theta - y_1 \cos 2\theta + y_2) \sin (2\theta - \alpha) + (x_1 \cos 2\theta + y_1 \sin 2\theta + x_2) \cos (2\theta - \alpha) = 0. \quad (9)$$

Similarly, the second equation when combined with (3), (6), and (8) reduces to

$$x_1 \tan \beta \cos 2\theta + y_1 \tan \beta \sin 2\theta + x_2 \tan \beta + (z_1 - z_2) \sin (2\theta - \alpha) = 0. \quad (10)$$

Assuming, for the time being, that the trinomial coefficients in (9) do not vanish simultaneously and that (10) is not satisfied by having $\beta = 0$ and $z_1 - z_2 = 0$, the elimination of α and β from formulæ (5), (9), and (10) may be effected by the following operations. The square of (5) may be transformed into

$$\tan^2 \beta = [\sin^2 (\theta - \alpha) - \sin^2 \gamma] \csc^2 \gamma,$$

which is then equated to the expression for $\tan^2 \beta$ obtained directly from (10). Since $\theta - \alpha$ is identically the same as $(2\theta - \alpha) - \theta$ it follows that

$$\sin^2 (\theta - \alpha) = \tfrac{1}{2}(\tau^2 + \tau^2 \cos 2\theta - 2\tau \sin 2\theta + 1 - \cos 2\theta)(1 + \tau^2)^{-1},$$

where $\tau \equiv \tan (2\theta - \alpha)$. Consequently the equation resulting from the elimination of $\tan^2 \beta$ may be written as a rational function of τ, $\sin 2\theta$, and $\cos 2\theta$. Elimination of τ is accomplished at once by substitution of τ from (9). The equation finally obtained is of the form

$$2A \sin 2\theta + B \cos 2\theta + C = 0,$$

where

$$A \equiv x_1 y_1 + x_2 y_2 + (x_1 y_2 + x_2 y_1) \cos 2\gamma,$$
$$B \equiv x_1^2 + x_2^2 - y_1^2 - y_2^2 + 2(x_1 x_2 - y_1 y_2) \cos 2\gamma,$$
$$C \equiv 2x_1 x_2 + 2y_1 y_2 - (z_1 - z_2)^2 + [x_1^2 + x_2^2 + y_1^2 + y_2^2 + (z_1 - z_2)^2] \cos 2\gamma.$$

Since $\sin 2\theta = 2t(1+t^2)^{-1}$ and $\cos 2\theta = (1-t^2)(1+t^2)^{-1}$, where $\equiv \tan\theta$, the last equation may be transformed into the following quadratic in the single unknown quantity t

$$\left.\begin{aligned} at^2 + 2bt + c &= 0, \\ a &\equiv (y_1+y_2)^2\cos^2\gamma - [(x_1-x_2)^2 + (z_1-z_2)^2]\sin^2\gamma, \\ b &\equiv (x_1+x_2)(y_1+y_2) - 2(x_1y_2 + x_2y_1)\sin^2\gamma, \\ c &\equiv (x_1+x_2)^2\cos^2\gamma - [(y_1-y_2)^2 + (z_1-z_2)^2]\sin^2\gamma. \end{aligned}\right\} \quad (11)$$

It should be remarked, in passing, that formula (11) may also be derived by making use of the fact that the reflected ray (extended backward) must pass through the virtual image of the point (x_1, y_1, z_1). As formula (11) is of the second degree, the conclusion may be drawn that, *in general, not more than two rays can be constructed when one point on the incident segment, one on the reflected segment, and the glancing-angle are given.* In applying the quadratic to numerical data it sometimes happens that one of the roots corresponds to a position of the mirror for which the points (x_1, y_1, z_1) and (x_2, y_2, z_2) are on opposite sides of the reflecting plane, thus causing one of the points to play the rôle of a virtual image. By equation (1), a necessary and sufficient condition for the points to lie on the same side of the plane is that $x_1 + ty_1$ and $x_2 + ty_2$ shall have like signs.

In the special case where both of the given points lie in a plane perpendicular to the axis of rotation ($z_1 = z_2$), the roots of (11) may be reduced to the following rational form

$$t = \mp\frac{(x_1+x_2)\cos\gamma \mp (y_1-y_2)\sin\gamma}{(x_1-x_2)\sin\gamma \pm (y_1+y_2)\cos\gamma}, \quad (11')$$

in which the upper signs, or the lower ones, must be taken together.[1]

Point Source and Negligible Penetration.—The special case of rays lying in a plane perpendicular to the axis of rotation of the mirror will next be considered. This condition is represented by $\beta = 0$ and $z_1 - z_2 = 0$, hence formula (10) is satisfied irrespective of the (finite) values of x_1, x_2, y_1, α, and θ. The admissible solutions of (5) are now $\theta_1 = \alpha + \gamma$ and $\theta_2 = \pi - (\gamma - \alpha)$. Equation (9) reduces to

$$(x \mp y_1\sin 2\gamma)\cos(2\gamma \pm \alpha) \pm (y + y_1\cos 2\gamma)\sin(2\gamma \pm \alpha) = 0, \quad (12)$$

in which the subscripts 2 have been suppressed, x_1 has been put equal to zero for sake of simplicity, and the upper and lower signs correspond respectively to θ_1 and θ_2. As may be seen at a glance, the lines represented by the upper and lower equations of (12) always pass respectively

[1] The order of the signs corresponds to $t = (-b \pm \sqrt{b^2 - ac})/a$.

through the points $(\pm y_1 \sin 2\gamma, \ -y_1 \cos 2\gamma)$ independently of α. Therefore, *all rays lying in a plane perpendicular to the axis of rotation of a plane selective mirror—the axis coinciding with the mirror (pure rotation)—and radiating from a single point will, after reflection, pass through two focal points each of which is at the same distance from the axis as the radiant point, the angles of deviation of the axial or principal rays of the pencils being numerically equal to twice the constant glancing-angle.* This fundamental theorem is not new, since demonstrations involving only elementary, non-analytic geometry have been given by Bragg, E. Wagner, and others. Nevertheless I have not seen a published proof which involves a concise, formal statement of the special conditions under which the theorem is valid. The limitations may have been fully appreciated, but they seem to have been tacitly assumed.

By taking the sum of the squares of the corresponding members of the equations

$$-x_2 = x_1 \cos 2\theta + y_1 \sin 2\theta,$$

$$-y_2 = x_1 \sin 2\theta - y_1 \cos 2\theta,$$

it will be found immediately that

$$x_2^2 + y_2^2 = x_1^2 + y_1^2.$$

Therefore as γ varies, the image point (x_2, y_2) describes the circumference of the focal circle having the radius $\sqrt{x_1^2 + y_1^2}$.

Point Source and Appreciable Penetration.—The qualifying remark, between the dashes in the last italicized sentence, will now receive attention. The pertinence of the question depends on the fact that, in general, X-rays penetrate to a finite depth into the diffracting crystal, so that rigorously not more than one plane of atoms can contain the axis of rotation. If this plane is the mean effective one then the parallel active planes must be situated on both sides of the axis and at different distances from the same. The problem is, accordingly: To investigate the properties of rays lying in a plane perpendicular to the axis of rotation when this axis is parallel to the reflecting surface, but does not coincide with the surface.

In Fig. 3, S $(a, 0)$ is the radiant point. The axis of rotation and the plane of the mirror are both perpendicular to the plane XOY, and they intersect it in the point O and the line $\overline{MN}$, respectively. Let p symbolize the length of the normal $\overline{OF'}$ dropped from O on $\overline{MN}$, and let this perpendicular make an angle α' with the direction $\overline{OX}$. The equation of the mirror is

$$\cos \alpha' \cdot x + \sin \alpha' \cdot y - p = 0.$$

The equation of the line joining S to its virtual image S' is

$$y = (x - a) \tan \alpha'$$

hence, the coördinates of the foot of the perpendicular F dropped from S on $\overline{MN}$ are

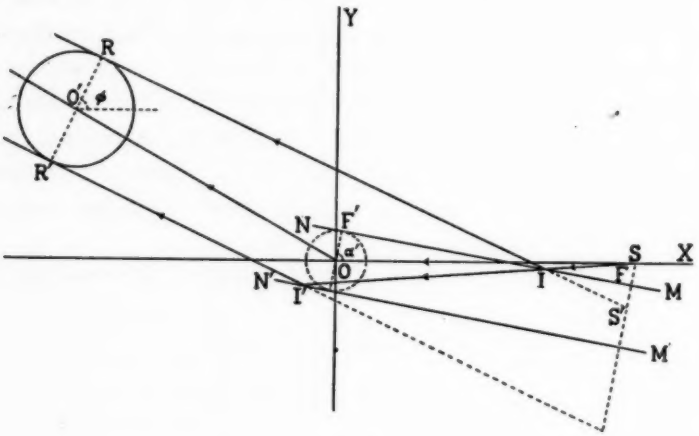

Fig. 3.

$$x' = p \cos \alpha' + a \sin^2 \alpha',$$

$$y' = (p - a \cos \alpha') \sin \alpha'.$$

Since $\overline{S'F} = \overline{FS}$ the coördinates of S' are found to be

$$x'' = 2p \cos \alpha' - a \cos 2\alpha',$$

$$y'' = 2(p - a \cos \alpha') \sin \alpha'.$$

The angle which the reflected ray makes with $\overline{OX}$ equals $(\pi/2) + \alpha' - \gamma$. Therefore the equation of the reflected ray $\overline{IR}$ is

$$\cos (\alpha' - \gamma) \cdot x + \sin (\alpha' - \gamma) \cdot y + a \cos (\alpha' + \gamma) - 2p \cos \gamma = 0. \quad (13)$$

Differentiation of equation (13) with respect to α' gives

$$\sin (\alpha' - \gamma) \cdot x - \cos (\alpha' - \gamma) \cdot y + a \sin (\alpha' + \gamma) = 0. \quad (14)$$

The envelope of the reflected ray is found at once by eliminating α' from the last two equations. (13) and (14) may be written as

$$A \sin \alpha' + B \cos \alpha' = C$$

and

$$B \sin \alpha' - A \cos \alpha' = 0,$$

where

$$A \equiv \sin \gamma \cdot x + \cos \gamma \cdot y - a \sin \gamma,$$

$$B \equiv \cos \gamma \cdot x - \sin \gamma \cdot y + a \cos \gamma,$$

and

$$C \equiv 2p \cos \gamma.$$

On squaring and adding the abbreviated equations, it is found that

$$A^2 + B^2 = C^2$$

or

$$(x + a \cos 2\gamma)^2 + (y - a \sin 2\gamma)^2 = (2p \cos \gamma)^2. \qquad (15)$$

Accordingly, *the complete envelope is the circumference of a circle having the radius* $2p \cos \gamma$ *and its center at the point* O' $(-a \cos 2\gamma, a \sin 2\gamma)$, which is identical in position with the focal point corresponding to $p = 0$. Formula (15) suffers no modification when the source S and the axis of rotation are on the same side of the mirror, that is, when the axis is in front of the reflecting plane instead of behind it.

The general nature and rational form of the preceding equations, together with the unlimited area of the reflecting surface, enable the analytical conditions to be fulfilled by points situated on reversed prolongations of the lines. Such points are formally correct but they do not correspond to the actual paths of the X-rays. As some portions of the envelope may also fail to satisfy the practical requirements of the problem, and since the radius of the circle is not negligible for penetrating radiations, it becomes necessary to examine in detail the properties of this locus.

The coördinates of the point of contact R of the reflected ray with the circle are easily derived from (13) and (15). They are

$$\left.\begin{aligned} x_e &= -a \cos 2\gamma + 2p \cos \gamma \cos (\alpha' - \gamma) \\ y_e &= a \sin 2\gamma + 2p \cos \gamma \sin (\alpha' - \gamma) \end{aligned}\right\}. \qquad (16)$$

Let ϕ denote the angle made by the radius to the point of contact $\overline{O'R}$ with the direction $\overline{OX}$. Then

$$\tan \phi = \frac{y_e - a \sin 2\gamma}{x_e + a \cos 2\gamma};$$

hence, by (16), $\tan \phi = \tan (\alpha' - \gamma)$; therefore

$$\phi = \alpha' - \gamma.$$

This simple relation is very helpful in following the motion of the point R when that of the point F' is known.

Now let another reflecting plane $M'N'$, which is parallel to MN and at the same numerical distance p from O, be taken into consideration. Assuming γ to have the same value for the plane $M'N'$ as for MN, the

coördinates of the point of contact R' may be found either by changing α' to $\pi + \alpha'$ or p to $-p$ in formulæ (16). Consequently

$$\tfrac{1}{2}(x_e + x_e') = -a \cos 2\gamma,$$
$$\tfrac{1}{2}(y_e + y_e') = a \sin 2\gamma,$$

and these are the coördinates of the center O' of the envelope. In other words, under the specified conditions, the points of contact are situated at the extremities of the same diameter. It is easy to show that the points S, I, and I' are collinear, so that both reflected rays arise from one incident ray.

A fair approximation to the circumstances pertaining to a real crystal may be made by imagining the space between MN and $M'N'$ to be filled with pairs of symmetrically situated reflecting planes for which p varies continuously (grating-spaces are of the order 3×10^{-8} cm.) from zero to a maximum value. To each pair of planes will correspond a little circular envelope, so that the entire area enclosed by the largest circumference will be crossed by the X-rays. It is therefore evident that, when the medial effective reflecting plane of the crystal coincides with the axis of rotation, the image of a *point source* will not be displaced laterally with respect to the ideal image O', which corresponds to negligible penetration. On the other hand, if the average reflecting plane is sufficiently eccentric, the image may be displaced enough to influence very accurate experimental work. Obviously, this displacement may be on either side of the axial ray $\overline{OO'}$.

Attention should also be called to the radius of the envelope $2p \cos \gamma$. As the X-rays become harder (shorter wave-length), not only does the maximum value of p become greater but the glancing-angle γ decreases, thus causing $\cos \gamma$ to increase. Hence, the radius is increased by both of its variable factors. Theoretically, therefore, this is unfortunate since the images become broader as the experimental difficulties inherent in the usual methods of determining glancing-angles increase.

The preceding analysis and deductions are subject to such qualifications as may arise from the finite width of the crystal face, the distance of the source S from O, etc. For example, by combining the equation of the mirror with formula (13), the coördinates of the point of incidence I are found to be

$$x_i = [p \sin (\alpha' + \gamma) - a \sin \alpha' \cos (\alpha' + \gamma)] \csc \gamma,$$
$$y_i = (a \cos \alpha' - p) \csc \gamma \cos (\alpha' + \gamma).$$

The point F' being $(p \cos \alpha', p \sin \alpha')$, the distance from F' to I is given

by

$$\delta = [p \cos \gamma - a \cos (\alpha' + \gamma)] \csc \gamma. \qquad (17)$$

Evidently the rotation of the crystal must not cause this quantity to vary over a greater range than the width of the face of the crystal.

Broadening of Image by Oblique Rays.—As the effect of the altitude angle β can be illustrated in a very large number of ways it becomes necessary to choose some specific case when quantitative data are desired. Accordingly, the following special problem has been selected for the reasons that it is relatively simple, and that it conforms closely to the experimental conditions which obtain when the ionization method is used, or when the photographic plate is placed normal to the axis of the beam of X-rays.

In Fig. 4, the line $\overline{ST}$, parallel to $\overline{OZ}$, may be looked upon as a slit of negligible width. Let the point S be $(0, y_1, -h)$. P indicates any point on the focal circle (assuming no penetration and no eccentricity) having the radius $\overline{OT} = y_1$. By hypothesis, the reflected ray $\overline{IR}$ is required to pass through P $(x_2, y_2, 0)$. In general, as the angle β varies, the point P will move around the circumference of the focal circle, and the arc passed over will correspond to the width of the image which would be recorded on a photographic film wrapped in the form of a circular cylinder, having $\overline{OZ}$ for axis and y_1 as radius. Before proceeding to numerical quantities, two simple algebraic relations must be derived.

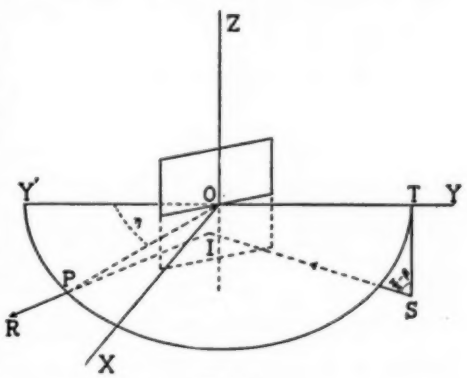

Fig. 4.

Since $x_1 = z_2 = 0$ and $z_1 = -h$, formula (10) reduces to

$$x_2 = h \cot \beta \sin (2\theta - \alpha) - y_1 \sin 2\theta$$

which, when substituted in equation (9), leads to

$$y_2 = y_1 \cos 2\theta - h \cot \beta \cos (2\theta - \alpha).$$

Substitution of these expressions in the equation of the focal circle

$$x_2^2 + y_2^2 = y_1^2$$

gives

$$h = 2y_1 \cos \alpha \tan \beta. \qquad (18)$$

In order to compare different positions of the point P, as this intersection moves along the circular arc, it is necessary to find a connection between the angle $Y'OP$ (η) and known quantities. Replacing $h \cot \beta$ by its equal $2y_1 \cos \alpha$ in the preceding simplified formulæ for x_2 and y_2, and noting that $2\theta = (2\theta - \alpha) + \alpha$, it will be found that

$$x_2 = y_1 \sin 2(\theta - \alpha),$$

$$-y_2 = y_1 \cos 2(\theta - \alpha).$$

But

$$\tan \eta = \frac{x_2}{-y_2}$$

hence

$$\eta = 2(\theta - \alpha).$$

Therefore, under the given conditions, η is equal to the deviation of the orthogonal projection on the plane XOY of the ray SIR. (See $\angle POQ$, Fig. 2).

Finally, by formula (5),

$$\sin \tfrac{1}{2}\eta = \frac{\sin \gamma}{\cos \beta} \qquad (19)^1$$

This equation shows that η has a minimum value when $\beta = 0$, hence, for slits of *zero width*, settings should be made on the *inferior edge* of a photographic image in order to obtain the correct value of the glancing-angle ($\eta_0 = 2\gamma$, $\beta = 0$).

The data for η_0, and h, in Table I., were calculated from the arbitrary values of β_0 given in the first column, α being assigned the value zero throughout. In all cases $\gamma = 15°$ and $y_1 = 10$ cm.

TABLE I.

β_0.	η_0.	h (mm.).
0° 0′	30° 0′ 0″	0
0° 30′	30° 0′ 4″	1.745
1° 0′	30° 0′ 17″	3.491
1° 30′	30° 0′ 38″	5.237
2° 0′	30° 1′ 7″	6.984
2° 30′	30° 1′ 45″	8.732
3° 0′	30° 2′ 32″	10.482

[1] It is interesting to note that this equation is identical in form and meaning with the relation $\sin \frac{1}{2}D = \sin \frac{1}{2}E \cos \eta_1$ which occurs in the theory of oblique *refraction* through prisms. Therefore, it is an expression of the single fact common to the laws of reflection and single refraction, which is, that the angles of incidence and reflection or refraction lie in the same plane containing the normal. See, H. S. Uhler, On the Deviation Produced by Prisms, Amer. Jour. Science, Vol. 35, p. 389 (1913).

The second column shows quantitatively how the point P (Fig. 4) moves along the circumference as β_0 receives equal increments, α remaining unchanged. The second differences for η_0 are practically constant. The third column[1] indicates the point on the slit through which the ray must pass in order to give the corresponding value of η_0.

If the image on a photographic film were of uniform density from one edge to the other, and if settings were made on the middle of the image, the error in the glancing angle would amount to + 0.03 per cent., for $\beta_0 = 2°\ 0'$ and $\gamma = 15°$. Since 0.01 per cent. seems to be attainable, the angular subtense of the total length of the slit at the center of the crystal should not exceed 3° when very accurate data are sought experimentally.

TABLE II.

h (mm.).	$\pm\ \alpha$.	θ_+.	θ_-.
1.048156	15° 1′ 10″	30° 2′ 31″	0° 0′ 11″
1.049	14° 50′ 47″	29° 52′ 9″	0° 10′ 34″
1.050	14° 38′ 21″	29° 39′ 42″	0° 23′ 1″
1.060	12° 22′ 44″	27° 24′ 5″	2° 38′ 38″
1.070	9° 36′ 37″	24° 37′ 58″	5° 24′ 45″
1.080	5° 37′ 37″	20° 38′ 59″	9° 23′ 44″
1.085	1° 10′ 43″	16° 12′ 4″	13° 50′ 39″
1.0852	0° 25′ 24″	15° 26′ 45″	14° 35′ 57″

Table II. is intended primarily to illustrate the fact that, *as the crystal is rotated*, different points along the slit send rays through a given point on the focal circle. Since, in formula (18), α is operated on by the cosine its sign cannot affect the values of the remaining quantities. In other words, two rays, having the same angular altitude β, can come from a given point of the slit and pass, after reflection, through a properly chosen, fixed point on the focal locus. The rays of such a pair have numerically equal values of α but different arithmetical values of θ, the position angle of the reflecting plane. As β changes sign so also will h do likewise [by (18)] so that two points on the slit and equidistant from the center of the same will simultaneously send two rays through the chosen focal point. Hence, for a given numerical value of β, four rays can diverge from the slit and, as the crystal is rotated, eventually converge to a single point on the focal circumference. It should be emphasized, however, that only finite segments of the slit can come into play in any actual case, since the angular positions of the reflector are theoretically limited by the condition that both the radiant point and the image point must lie on the same side of the crystal. (In

[1] Units are given to fix the ideas. The angles only determine the *ratio* h/y_1.

general, the horizontal width of the crystal would restrict the length of the effective slit segment more than the formal limiting condition just mentioned.) If the rays be reversed, so as to treat the fixed point on the focal circle as source and the slit as an image locus, then the properties under discussion amount to a sort of astigmatism.

In Table II., $y_1 = 10$ cm., $x_2 = 5.00683$ cm., $y_2 = -8.65631$ cm., $\beta = 3° 6' 21''$, $\gamma = 15° 0' 0''$, and $\eta = 30° 2' 43''$.

In applying photographic processes to the accurate determination of the glancing-angles (with respect to a definite kind of crystal) of characteristic X-rays it is not always convenient or desirable to place the plate either normal to the axis of the beam of rays or as a mean chord for a narrow region of wave-lengths. (Photographic *films* are unreliable for quantitative work.) Instead, the plate is placed normal to the line which passes through the center of the slit and intersects the axis of rotation at right angles. For sake of brevity, this line will be called the " collimation line." In this method care is usually taken to have the distance from the axis to the latent image equal to the distance from the slit to the axis, in order to take advantage of the uniplanar focal properties discussed above. For this case also, I have investigated, both analytically and arithmetically, the broadening of the photographic impressions due to the angular altitude β. Even when α is kept equal to zero the datum finally required depends upon the solution of a cubic. It would be superfluous, therefore, to reproduce the analysis and numerical data in this place. Suffice it to state that, as might be expected, the displacement of the center of the image is greater here than in the hypothetical case of a cylindrical film previously treated. The relative increase in displacement is primarily due to the changing azimuthal obliquity of the rays with respect to the normal to the photographic plate. An approximate idea of the conditions prevailing in the present problem may be formed by referring to Fig. 4 and imagining the plate to be represented by a plane parallel to XOZ and passing through the point P, when η has its least value 2γ. In all cases, the effect of β is to give too large a value for the apparent glancing-angle and hence to produce a positive error in the computed wave-length.

In all of the preceding cases the hypothesis was made that the reflecting planes were parallel to the axis of rotation. Even when the incident rays lie in the plane YOZ (Fig. 1) and are parallel to $\overline{YO}$, an effective obliquity is produced when the normal $\overline{ON}$ describes, during the rotation of the crystal, a cone having $O\overline{Z}$ as axis. As a consequence of the canting of the crystal the line on the spectrogram lacks parallelism to the central image formed by the undeviated rays. Even if it were possible

to measure the plate along the line in which it was intersected by the plane containing the collimation line and normal to the axis of rotation, the distance obtained would not be exactly correct, so that a slight error might be introduced in the calculated value of the glancing-angle.

The equation of the spectral line corresponding to the ideally simple conditions specified in the preceding paragraph will now be given without proof. It is

$$(1 - 2\cos^2\theta\cos^2\phi')x' - \cos\theta\sin 2\phi'\cdot z' + \sin 2\theta\cdot\cos^2\phi'\cdot y_0 = 0. \quad (20)$$

The plane of the plate is expressed by $y = -y_0$. (Reference may be made to Fig. 1.) The origin of coördinates is taken on the collimation line. The axes of x' and z' lie in the plate and are parallel respectively to $\overline{OX}$ and $\overline{OZ}$. ϕ' denotes the angle which the normal $\overline{ON}$ makes with its orthogonal projection on the plane XOY. It is counted positive when the complementary angle ZON is acute, that is, when the top of the crystal is tilted back from the axis of rotation. θ symbolizes the angle which this projection makes with the axis $\overline{OX}$. Formula (20) may be freed from the auxiliary angle θ by virtue of the relation

$$\sin\theta = \sin\gamma\sec\phi'.$$

The linear equation may be employed in two different ways. (*a*) By properly superposing two spectrograms, so as to magnify the angular error, an approximate value of the slope of the spectral line can be obtained. Equating the numerical value of this "slope" to its algebraic expression derived from (20), an estimate of ϕ' may be gotten at once by solving the resulting quadratic in $\cos 2\phi'$. (*b*) The intercept on the axis of x', derived from formula (20), may be employed in calculating the order of magnitude of the error introduced by the maladjustment of the crystal.

Assuming $y_1 = 10$ cm., $\gamma = 15°$, and $\phi' = 1°$, the values of the remaining quantities were computed to be: $x_0 = 5$ cm., $y_0 = 5\sqrt{3}$ cm., $\theta = 15°\,0'\,8''$, slope angle $= 92°\,13'\,5\bar{1}''$, and intercept on x' axis $= 5.0027$ cm. Therefore, the spectral image slants in the same general direction as the crystal face and makes an angle of $2°\,13'\,5\bar{1}''$ with the vertical. This angle exceeds $2\phi'$ by 11.5 per cent. The linear displacement along the plate equals 0.027 mm. The calculated glancing-angle would be $15°\,0'\,24''$, which corresponds to an error of $+0.045$ per cent. My short practical experience with the determination of glancing-angles leads me to believe that, in the vicinity of 15°, it is possible to attain an appreciably higher degree of accuracy than 1/22 per cent.

Practical Deductions.—In the first place, the preceding discussion of

the asymmetric broadening of spectral images due to obliquity in angular altitude leads to the conclusion that, when the highest attainable accuracy is required, diaphragms should be used so as to limit the vertical height of the incident beam of *X*-rays. Probably the most advantageous location of one of the diaphragms would be (in the case of primary rays) on the side of the anticathode itself. Although all the cases treated analytically involved the assumption that the slits were of zero width, it seems obvious that the various errors will not be decreased when the slits have the finite horizontal aperture necessary for the practical transmission of energy. In the following paragraphs, therefore, the hypothesis will be made that the rays do not depart appreciably from planes perpendicular to the axis of rotation.

In the usual photographic method of determining glancing-angles it is necessary to measure the perpendicular distance from the axis of rotation to the plate. It is very difficult, if not impossible, so to adjust the apparatus as to satisfy the definition of this distance, for, in the case of rays of sensible penetration, the *mean* effective reflecting plane, which should contain the axis of rotation, lies at a depth from the front face of the crystal that involves uncertainty. Even if the crystal were in perfect adjustment for one particular wave-length it would not remain so for rays of appreciably different penetration. Doubt also arises as to whether the gelatin side of the plate always clamps at the same distance from the axis of rotation, no matter how rigid the plate-holder itself may be. (Gelatin is compressible, commercial dry plates are very often curved and twisted, etc.)

The errors arising from these, and from many other, causes may be largely, if not entirely, eliminated by the "Method of Displacement." As far as I can find from the literature of the subject this simple idea is new. It consists in taking one exposure when the plate is at a certain distance from the crystal and then a second exposure when it is at a different distance from the reflector. The displacement of the spectral image, corresponding to some one wave-length, is a function of the distance through which the plate has been *translated* parallel to the collimation line. The form of the function and the details of the calculation of the glancing-angle depend respectively upon the value of the constant angle between the normal to the plate and the collimation line, and upon whether the measurements are absolute or are based upon adjacent images pertaining to known wave-lengths. The interval of translation may be determined with ease and great accuracy, whereas only an approximate value of the distance between the plate and the axis of rotation is required in any case. The plate can be pressed suf-

ficiently flat by strong springs and, as it cannot move relative to its holder, no doubt can arise concerning the distance through which the plate has been translated. On the other hand, the method of displacement involves the fundamental assumption that the images of the same spectral line are sensibly identical in the two positions of the plate-holder. As far as I have been able to find, both theoretically and experimentally, this assumption is fulfilled by using *two narrow slits of exactly the same width.* (Obviously, both slits must be completely filled by the beam of X-rays.)

The formation of a beam of X-rays of constant cross-section, by two slits of identical opening, will now be explained. As stated before, it will be assumed that diaphragms have been interposed in the path of the beam in such a manner as practically to eliminate any asymmetric broadening of the images due to the angular altitude β. For the time being, the hypotheses will also be made that there is no penetration and that the reflecting plane contains the axis of rotation. On the contrary, the assumption that the slits are of zero width will no longer be retained.

The plane of the diagram (Fig. 5) is taken normal to the mutually

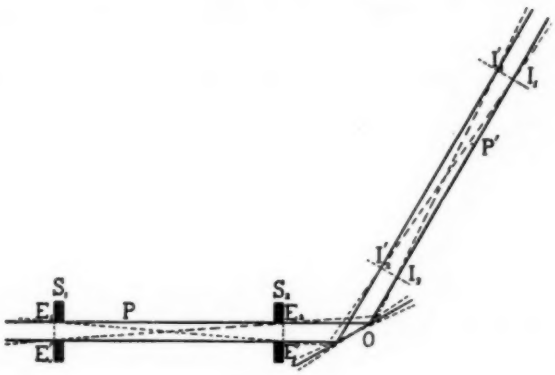

Fig. 5.

parallel long-axes of the slits S_1 and S_2, but it does not have to contain the collimation line. Now, by the fundamental theorem of the focal circle (or cylinder), any ray which passes through the incidence edge E_1 of slit S_1 will, after reflection from the crystal at the given glancing-angle γ (monochromatic radiation being assumed), pass through the point I_1. The point I_1 is at the same distance from the axis of rotation O as the point E_1, and the deviation of the line $\overline{OI_1}$ with respect to the line $\overline{E_1O}$ equals 2γ. The ray in question is not required to strike the crystal at the point O. If the ray also passes through the emergence

edge E_2' of slit S_2 it will, after reflection, pass through a point I_2'. This point is likewise determined by the conditions $\overline{OI_2'} = \overline{E_2'O}$ and $\angle E_2'OI_2' = \pi - 2\gamma$. Hence, one extreme diagonal ray $\overline{E_1E_2'}$ takes the direction $\overline{I_2'I_1}$ after reflection. Similarly the incident rays $\overline{E_1'E_2}$, $\overline{E_1E_2}$, and $\overline{E_1'E_2'}$ will become the reflected rays $\overline{I_2I_1'}$, $\overline{I_2I_1}$, and $\overline{I_2'I_1'}$, respectively. In general, therefore, a ray which passes through *any* point P ***within*** the rectangle $E_1E_2E_2'E_1'$ will, after selective reflection, pass through the homologous image point P', such that $\overline{OP'} = \overline{PO}$ and $\angle POP' = \pi - 2\gamma$. Since all rays that pass between the jaws of both slits are confined between the parallel segments $\overline{E_1E_2}$ and $\overline{E_1'E_2'}$ it follows at once that the reflected beam cannot escape through the sides $\overline{I_2I_1}$ and $\overline{I_2'I_1'}$ of the rectangle $I_1I_2I_2'I_1'$. Consequently as long as the gelatin side of a plate is moved parallel to itself (along the collimation line or in some other direction), and is kept within the limits set by the condition that the sensitized surface shall not intersect the reflected beam at any point outside of the rectangle $I_1I_2I_2'I_1'$, the images will be of constant width, and their relative shifts will be directly proportional to the displacement of the plate. As the length of the rectangle $\overline{I_2I_1}$ is equal to the constant distance $\overline{E_1E_2}$ between the slits it is independent of the glancing-angle involved. Hence, the length $\overline{I_2I_1}$ is dependent neither upon the wave-length of the X-rays nor upon the grating-space of the crystal. On the contrary, the projection of $\overline{I_2I_1}$ on the collimation line is a function of the glancing-angle. In particular, if the photographic plate is kept normal to this line the interval of translation is a little less than $\overline{I_2I_1} \cos 2\gamma$.

If all the incident rays were strictly parallel to $\overline{E_1E_2}$ then all of the reflected rays would be exactly parallel to $\overline{I_2I_1}$, the beam would experience reflection for only one angular position of the crystal (assuming that the curve of reflection is extremely steep on both sides of the maximum), and nothing would be gained by rotating the crystal. These conditions would be fulfilled quite independently of penetration and of any eccentricity of the mean effective reflecting plane. By drawing lines, representing traces of planes, parallel to the lines which pass through O (Fig. 5) and which indicate three positions of the single non-eccentric reflecting plane, it is easy to see that the effects of symmetrical penetration and of eccentricity would be respectively to increase the cross-sections $\overline{I_1I_1'}$ and $\overline{I_2I_2'}$, and to shift the principal axis of the reflected beam parallel to itself. [The rays $\overline{IR}$ and $\overline{I'R'}$ (Fig. 3) are parallel and arise from the single incident ray $\overline{SII'}$.] Simple displacement without alteration either in direction or in constancy of cross-section would have no influence on the present method of determining glancing-angles. Hence, all restricting conditions, save β negligible, have been removed.

The method has been tested experimentally, by Dr. C. D. Cooksey[1] and myself, for the fairly soft rays of the K series of gallium and of the L series of tungsten, and found to be very convenient and accurate. We have not had time, as yet, to try it with very penetrating X-rays. If, for some unforeseen reason, the scheme of using two equal slits simultaneously should eventually be found unsatisfactory for very hard rays, the method of displacement may still be applied by using slit S_1 alone when the plate is near the focal spot I_1I_1', and then employing slit S_2 alone with the plate near I_2I_2'. The last application of the general method might require especially accurate construction and adjustment of the spectrograph, but it would retain all the desirable features (such as intensity) of the usual method of experimentation together with the great advantage of knowing precisely how far the plate has been translated.

Summary.

1. The general equations of incident and reflected rays have been derived.

2. It has been demonstrated that, in general, not more than two rays are determined by one point on the incident segment, one point on the reflected segment, and the glancing-angle.

3. The special theorem of the focal circle has been stated and proved in a perfectly general manner. It has been shown that this theorem involves the following assumptions: (*a*) The rays of a pencil must all lie in one plane perpendicular to the axis of rotation of the crystal, (*b*) the rays must not penetrate the crystal to a finite depth, (*c*) the reflecting plane must contain the axis of rotation, and (*d*) the slit must act as a mathematical line source.

4. It has been shown analytically that a circular envelope arises when the reflecting plane is parallel to the axis of rotation, but does not contain this axis. Special properties of this locus have been demonstrated.

5. It has been proved that rays having finite angular altitude produce asymmetric broadening of the spectral images even when the azimuth is zero. It has been shown that, when the angular altitude is constant and the azimuth is finite and variable, the bundles of rays have astigmatic properties. The fact that this broadening is always in such a direction as to lead to too large a value of the glancing-angle has been demonstrated. The special case of a photographic plate normal to the line of collimation has been discussed.

6. The results obtained from an analytical study of the alteration in

[1] See "The K Series of the X-Ray Spectrum of Gallium," by H. S. Uhler and C. D. Cooksey, PHY. REV., N.S., p. 645, vol. X., Dec., 1917.

the slope and intercepts of a spectral line, due to tilting the reflecting planes of atoms with respect to the axis of rotation, have been given.

7. Whenever possible, the practical bearing of the theoretical considerations has been discussed. In particular, the theoretical and experimental aspects of a supposedly new method for the accurate determination of glancing-angles have been presented at some length. In so doing, slits of *finite* width and rays of sensible penetration have been considered. The general method involved has been styled the "Method of Displacement," and two ways of applying it have been suggested. One of these ways has been tested experimentally and found very convenient and accurate.

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THE RATIO OF THE INTENSITIES OF THE D LINES OF SODIUM.

BY VIVIAN VOSS.

IT has been known for a long time that the ratio of the intensities of the D lines varies with the intensity of the sodium flame.

Gouy[1] found the ratio D_2/D_1 to vary from 1.3 for a strong flame to 2 for a weak flame.

An investigation by Brotherus[2] showed that the ratio varied from 1.25 to 1.53.

Some observations made by Wood[3] indicated that, for an exceedingly weak flame, the ratio attained a value as high as 3 or 3.5. The estimate was made by comparing photographs made with different times of exposure, and it was assumed that the blackening of the photographic plate was directly proportional to the time of exposure.

This large value of the ratio was questioned in a recent paper by Ladenburg,[4] and so, at the suggestion of Professor Wood, a more careful investigation was made.

In the present work, three methods have been employed:

(*a*) A photographic method, based on the use of a sectored disc.

(*b*) A visual method in which the intensities were made equal by a polarization method.

(*c*) A visual method in which screens, having known coefficients of absorption, were used.

We shall consider first the photographic method.—A sectored disc (Fig. 1) was prepared, for which the ratio of the time of exposure of any element to that of the next adjacent element was 5/4. The disc was backed by a large flame from a Meker burner, and an image of the upper portion of the disc sharply focused on the slit of a large plane-grating spectrograph. The flame was charged with sodium and the slit of the spectrograph opened until the rectangular images representing the two wave-lengths D_2 and D_1 just touched. If, now, the disc was set in rota-

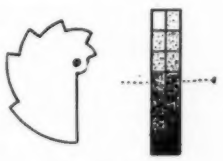


Fig. 1.

[1] G. Gouy, Ann. de Chem. et de Phys., 18, 5, 1879.

[2] Hj. V. Brotherus, Ann. der Phys., 38, 397, 1912.

[3] R. W. Wood, Phys. Zeit., 15, 382, 1914.

[4] R. Ladenburg, Ber. der Deut. Phys. Ges., 12, 765, 1914.

tion by a small motor, the lines were cut into seven horizontal strips of varying, integrated intensity.

To obtain the maximum value of the ratio, it is necessary to work with a flame of much less intensity than any commonly employed in the laboratory. The easiest method of obtaining such a flame is to charge the air of the room with sodium by operating a rather intense sodium flame for a few minutes. As the work was carried out in a large room, and the doors and windows were kept shut, it was possible to obtain in this way a very feeble flame which remained practically constant for an hour or more. It is important to have the grid of the Meker burner perfectly clean, and the air should be free from dust, for if this is present the particles make bright flashes of sodium light as they pass through the flame. These flashes are many times brighter than the feeble flames with which the large ratios are obtained. By avoiding unnecessary movement in the room after the dust particles had been allowed to settle, the number of flashes could be reduced. With a very intense flame the plate was exposed for three seconds, while forty minutes were required in the case of a very feeble flame. This makes the ratio of the extreme flame intensities somewhat less than 1 : 800. The intensity ratio D_2/D_1 was determined for a given plate by picking out the two exposures (horizontal strips) for one of which D_2 showed the same photographic density as that of D_1 on the other.

The sectored disc was rotated at a very slow speed,[1] and it was at first assumed that the density of the image on the photographic plate was directly proportional to the time of exposure. On the above assumption, the ratio D_2/D_1 could be immediately determined as the inverse ratio of the times of exposure which made D_2 and D_1 equally black on the plate.

As no Hartmann photometer was available the comparisons were made by cutting the plate in two at the dotted line, Fig. 1, superposing the two halves, film to film, and matching D_2 on one piece against D_1 on the other, with the aid of a magnifying lens. This method is fairly accurate, as by carefully fitting the plates the dividing line between the two patches under examination can be made to disappear as in a photometer.

Preliminary work showed that an exposure ratio 5 : 4 could be easily detected in this way, and this ratio was accordingly adopted in making the sectored disc.

The intensity ratios that could be determined in this way were as follows:

1, 1.25, 1.56, 1.95, 2.44, 3.05, and 3.81.

[1] K. Schwarzschild, Astrophys. Jl., XI., 92, 1900.

Care was taken to avoid having any of the horizontal strips either under or over exposed.

With a very intense flame the ratio $D_2/D_1 = 1.25$ was obtained and with the feeblest flame $D_2/D_1 = 3$. This maximum value 3 was later shown to be too large, owing to a source of error in the photographic method which has not as yet been explained.

The decrease in the ratio with increasing flame intensity is due to the more powerful absorption of the D_2 light. That absorption may fully account for the effect was shown in the following way: The slit of a spectroscope was illuminated by a feeble sodium flame and opened, as before, until the two rectangles corresponding to D_1 and D_2 just touched. A glass bulb, highly exhausted and containing some sodium, was interposed between the flame and the slit, and the sodium was vaporized by playing a flame over the bulb. The large ratio for the weak flame immediately dropped to the smaller value found for a more intense flame. To get the maximum value of the ratio we should abolish absorption completely. We of course approximate this condition in a flame very lightly tinted with sodium, but if we could powerfully excite a very thin layer of the gas, the conditions would be still more favorable. Accordingly, a canal ray tube,[1] Fig. 2, was made. The cathode consisted of an aluminum disc, punched with numerous holes. The copper wire leading to this was insulated by a piece of thin glass tubing. The canal rays issuing from the holes in the cathode struck the lump of rock salt R, and in this way a highly luminous and exceedingly thin layer of sodium vapor was obtained. The ratio D_2/D_1 was no larger than for a very weak flame.

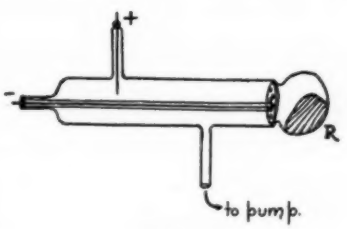


Fig. 2.

The same value of D_2/D_1 as for a feeble flame was also obtained by passing an electrodeless discharge through a vacuum tube containing sodium vapor. An image of the central capillary portion, which was about two millimeters in diameter, was thrown by a lens upon the slit of the spectrograph. The tube was heated to allow the discharge to

[1] If the tube is made of sodium glass, in the absence of the rock salt R a bright sodium fluorescence is obtained on the end of the tube on which the canal rays impinge. It was suspected that the extreme shallowness of the glowing layer might result from the circumstance that a thin layer of glowing sodium vapor is imprisoned by a layer of adsorbed air, and a test of this hypothesis was made by heating a small portion of the bulb, thus driving off the adsorbed air at that point. This region ceased to fluoresce though the rest of the bulb fluoresced brightly. On admitting air into the tube and allowing this to cool, the portion which had been heated gradually recovered its power of fluorescing.

pass, and a photograph of the D lines taken. An exposure of five minutes was necessary. The D_2 line on this plate was matched with a D_2 strip on one of the plates taken with the rotating sector and a weak flame. The D_1 line was found to match with the D_1 strip showing that the ratio was that obtained with a weak sodium flame.

Polarization Method.—The polarization method was next tried. Professor Wood's quartz block,[1] 32 mm. thick and cut parallel to the optic axis, was used.

If a beam of sodium light polarized in a plane making an angle of 45° with the optic axis (which is vertical) is passed through the block, the rays D_1 and D_2 on emergence will be polarized in mutually perpendicular planes. Either D_1 or D_2 can be extinguished by a Nicol prism properly oriented, and with the Nicol in some intermediate position D_1 and D_2 can be made of the same intensity. By observing the position of the Nicol when this condition obtains, the original intensity ratio can be computed.

For a full description of the block and its uses the reader is referred to Professor Wood's original paper. Light from a sodium flame was made parallel by a lens and passed through a Nicol prism, so that on emerging its direction of vibration made an angle of 45° with the vertical. It was then passed through the quartz block, through a second Nicol, and brought to a focus on a slit of the spectrograph by a lens.

The quartz block was first removed and the second Nicol crossed accurately with the first. The reading on the graduated circle of the second Nicol was then taken. The block was now introduced and rotated slightly about a vertical axis until D_1 was cut out. On turning the second Nicol through 90°, D_2 was cut out. Between these two positions there is one position for which the intensities of D_1 and D_2 can be made equal. If θ is the angle between this direction and the direction of vibration of D_2, then the ratio of the intensity of D_2 to that of D_1 is $\tan^2 \theta$. To obtain large values of the ratio, however, feeble flames must be used, and after passing through the Nicols the light is much reduced in intensity.

Some difficulty was experienced at first in making settings for the position of equality, but after much practice settings could be made which differed by less than two degrees. The mean of many readings was taken. The chief source of error lay in the setting of the first Nicol so that the light incident on the block was polarized in a plane making an angle of 45° with the optic axis. If this angle was less than 45°, on emerging from the block D_2 made an angle less than 90° with D_1 as can be seen from Fig. 3.

[1] R. W. Wood, Phil. Mag- 27, 524, 1914.

OD_1 represents the condition of vibration of incident light. It is analyzed by the block into OX and OY. On emergence the direction of vibration of D_1 is parallel to its original direction, but in the case of D_2, OX is rotated through 180° to OX', and the resultant direction of vibration is now parallel to OD_2, also making an angle ϕ with the optic axis. If ϕ is less than 45° the angle between OD_1 and OD_2 is less than 90°, and similarly if ϕ is greater than 45°, the angle is greater than 90°.

Now the ratio of the intensities D_2/D_1 is given by $\tan^2\theta$, where θ is the angle between the position of equality of the second Nicol and the direction of vibration of D_2.

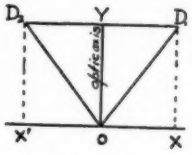


Fig. 3.

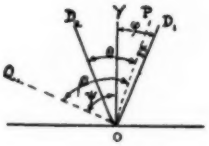


Fig. 4.

In Fig. 4, OD_1 and OD_2 represent the directions of vibration of D_1 and D_2 respectively. OP represents that position of the second Nicol for which D_1 and D_2 on emergence are of equal intensity. OQ is perpendicular to OD_1.

If $< 2\phi$ (Fig. 3) is less than or greater than 90°, $< 2\psi$ (Fig. 4) is greater than or less than 90°.

If, as in Fig. 4, $< 2\psi$ is greater than 90° the true value of the ratio D_2/D_1 is $\cos^2\alpha/\cos^2\theta$, while the measured ratio is

$$\tan^2\beta = \frac{\sin^2\beta}{\cos^2\beta} = \frac{\cos^2\alpha}{\cos^2\beta},$$

and is larger than the true ratio. Similarly, if $< 2\psi$ is less than 90° the measured ratio is too small. After the first Nicol had been set approximately, and the quartz block put in position, the second Nicol was turned until D_2 was cut out. It was found difficult to make this setting accurately owing to the small intensity of the light. The observed values of D_2/D_1 increased rapidly as 2ψ became greater than 90° and diminished rapidly for values of 2ψ less than 90°.

Values in the neighborhood of 2 were obtained for the ratio, with a flame colored only by the sodium in the air when the air was heavily charged with sodium vapor. Such a flame is fairly bright, though considerably less bright than a flame colored by an asbestos wick dipped in brine. As will be shown later, the value 2 was also obtained for such a flame by the third (most accurate) method employed.

For the feebler flames, burning in air only lightly charged with sodium, it was extremely difficult to make accurate settings. From one set of readings a value 2.3 was obtained for the ratio, while another set, under apparently identical conditions, gave a value 2.6. The readings of this latter set are given below:

Second Nicol Crossed with First.	D_2 Extinguished by Second Nicol.	Position of Equality of D_1 and D_2.
− 21°	70°	37°.3
− 22	67	36.2
− 21	68	36.8
− 21.5	70	37.6
− 21	66	37
− 21.8	71	37.5
Means − 21°.4	68°.7	37°.1

From these, $2\psi = 90°.1$ and $\theta = 58°.5$

$$\frac{D_2}{D_1} = \tan^2 \theta = 2.6.$$

This method can be used therefore for flames varying from very bright to fairly weak, but is unsuitable for the feeble flames.

The largest accurate value given by this method is 2 and is obtained for a flame burning in air strongly charged with sodium.

Visual Method.—The third method will now be discussed. Some gray gelatin films, whose coefficients of transmission had been determined to a tenth of one per cent., were supplied through the courtesy of Dr. Mees, of the Eastman Kodak Co. Narrow strips of these were cut and put across the plateholder of the large plane-grating spectrograph (Fig. 5). The strip *a* let through $33\frac{1}{3}$ per cent. of the incident light, *b*, 40 per cent. and *c*, 50 per cent.

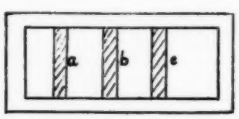


Fig. 5.

The slit of the spectrograph illuminated with sodium light was opened until the two rectangles corresponding to D_2 and D_1 just touched. By sliding the plateholder along, D_2 could be covered successively by *a*, *b*, or *c*, and values 3, $2\frac{1}{2}$ and 2 distinguished for the ratio D_2/D_1. When the air of the room was charged with sodium vapor, and the flame of a Meker burner put before the slit, D_2 and D_1 appeared of exactly the same intensity when D_2 was covered by *c*, the 50 per cent. screen. This was true for the fairly bright flames obtained in this way (and even these are considerably weaker than the flames colored by an asbestos wick dipped in brine), and also for the weaker, down to the very feeble flames. In every case the match was perfect.

Since it was easily possible to distinguish the difference in ratio when D_2 was covered by the 40 per cent. and by the 50 per cent. screens, it was estimated that the value 2 for the ratio D_2/D_1 was correct to within 10 per cent. This direct method is certainly the most reliable of the three.

Investigation of Apparent Inconsistency of Results of the First and Third Methods.—It was now necessary to investigate the inconsistency in the value 2 given in this method for the ratio in the weaker flames and the value 3 given by the first (photographic) method.

An oblong slit, 24 × 6 mm., was cut in a sheet of cardboard and covered with a yellow screen which cut off everything below the D lines. Half of this slit was covered with a strip of the 50 per cent. gelatin screen. This was backed first by a sodium flame and between the flame and the slit was placed a piece of uniformly diffusing ground glass. Photographs of the slit were now taken with varying times of exposure by means of an ordinary box camera. The photographs were all taken on the same plate by sliding the plate along in the plateholder between exposures. One set of times of exposure were as follows: 4, 8, 12, 16, 24, 36, and 4 seconds. The last exposure of 4 seconds was taken to determine whether the intensity of the flame had changed during the experiment. A constant flame was obtained by putting a small piece of sodium glass tubing on the grid of a Meker burner. The times of exposure were determined by the swings of a seconds pendulum. The plate was cut lengthwise, the two parts placed film to film, and the darker half of one strip was matched against the light half of another. In every case it was found that the ratio of the times of exposure of two half-images that matched was 3 : 1, exactly as had been obtained in the photographs with weak flames for D_1 and D_2 in the first method.

Great care was taken to have the density of the image uniform throughout the length of the strip, as otherwise an error would be made in matching the strips unless the match was made exactly at the dividing line.

The slit was now backed by a tungsten lamp placed behind a diffusing screen made of two sheets of ground glass and a set of exposures again made. The ratio of the times of exposure of the strips that now matched was 2 : 1. The difference in the effects obtained with a sodium flame and with a tungsten lamp cannot be due to a difference in the coefficient of transmission of the gelatin film for sodium light, for the yellow film placed over the artificial slit cut off everything below the D lines, and the sensitivity of the Cramer isochromatic plates used falls off rapidly above the D lines. This was further verified by illuminating the slit

with a very sharp continuous spectrum in the region of the D lines, obtained from a monochromator. In this case also the ratio of the times of exposure was 2 : 1.

It is also impossible to explain the difference by a variation with the wave-length, in the quantity k in Schwarzschild's equation for the blackening of the photographic plates, $S = It^k$ (S is the density of the image, I the intensity of the light, t the time of exposure, and k a quantity varying slightly with the plate used and the wave-length of light), owing to the very narrow range of wave-lengths used.

These results made it appear as if a curious difference existed between the behavior of the photographic plate towards white light and monochromatic light. This would bring the results obtained by the first method into perfect agreement with those obtained by the other two methods. For a ratio 3 for the times of exposure obtained with the sectored disc means a ratio of $D_2/D_1 = 2$.

A large number of experiments were made, all of which gave very nearly the same results. Dr. Mees has however failed to confirm them in the research laboratory of the Eastman Co. and the source of the discrepancy has not been located at the present time.

SUMMARY.

By three independent methods it has been shown that the maximum value for the ratio of the intensities of the D lines of sodium is $D_2/D_1 = 2$, correct to within 10 per cent.

In conclusion the author wishes to express his hearty thanks to Professor R. W. Wood for suggesting the problem to me and for the many suggestions made throughout the course of the investigation.

JOHNS HOPKINS UNIVERSITY,
June, 1917.

ON THE THERMODYNAMICS OF FLUORESCENCE.

By E. H. Kennard.

THE relationship between thermodynamics and fluorescence does not seem to have been investigated hitherto in as thorough a manner as the subject deserves. In the present paper the conclusions that can be obtained without adopting special hypotheses are first carried a little further than is done by Pringsheim[1] in his discussion of the subject, and a plausible hypothesis concerning the properties of the fluorescent process is then advanced and is found to lead to an interesting relationship between fluorescence and the black body spectrum which appears to be confirmed by experiment.

Throughout the paper it will be assumed that fluorescence is a reversible process, so that thermodynamic equilibrium is possible in a system containing a fluorescent substance.

I.

Let us first consider an isothermal enclosure containing an isotropic fluorescent substance. In the latter there will be set up the usual flux of radiation corresponding to the temperature of the enclosure; let J_1 denote the normal flux per unit of wave-length at wave-length λ_1. (J_1 is therefore the flux in vacuo multiplied by the square of the refractive index.) The existence of equilibrium now requires as usual that the radiant energy emitted by the substance shall be equal to that absorbed for each wave-length separately; but in the present case the emission consists in part of fluorescence. The latter may be denoted by

$$F_1 = \int_0^\infty f_{12} J_2 d\lambda_2, \tag{1}$$

where f_{12} is the "coefficient of fluorescence," *i. e.*, the fluorescent emission per unit volume and per unit wave-length at λ_1 which is excited by unit normal flux of wave-length λ_2; F_1 is thus the fluorescent emission excited by black body radiation at the temperature of the enclosure and may be called the *full fluorescent emission* corresponding to that temperature.

Hence, denoting by E_1 the intensity of thermal emission per unit volume at λ_1 and by a_1 the coefficient of absorption,

$$E_1 + F_1 = a_1 J_1. \tag{2}$$

[1] E. Pringsheim, *P. Z. S.*, XIV., p. 129, 1913.

Instead however of concluding, with Pringsheim, that Kirchhoff's law fails for fluorescent substances, it seems preferable to generalize the law itself as follows: *In different substances at the same temperature the absorption is proportional to the sum of the thermal and the full fluorescent emissions at each wave-length.*

It is more convenient, however, to think of the absorption as consisting of two parts:

$$a_1 = \alpha_1 + \beta_1,$$

where

$$\alpha_1 = E_1/J_1 \tag{3}$$

and is the coefficient of the "thermal absorption" which equilibrates the thermal emission, while

$$\beta_1 = F_1/J_1 \tag{4}$$

and is the coefficient of the "fluorescence absorption" which equilibrates the fluorescent emission in the enclosure. The distinction seems likely on general grounds to be a real one, but it may not be; nor can we say a priori whether the fluorescence absorption should be affected by the action of the exciting light—an effect which has been looked for repeatedly but without success.

We may now deduce certain conclusions applicable to an isolated fluorescing body. Let us suppose first that the exciting light is so adjusted that its spectrum is proportional in intensity at all wave-lengths to the black-body spectrum corresponding to the temperature of the fluorescing body. Let us assume further as an experimental fact that proportionality holds between fluorescence and exciting intensity. Then if F' denotes the intensity of fluorescent emission per unit volume, and J', the intensity of flux of the exciting light, the former will bear to full fluorescence the same ratio that the latter bears to black-body radiation, and by (4) we shall have for any wave-length λ_1

$$F_1' = \beta_1 J_1', \tag{5}$$

where all quantities are taken for the same wave-length.

Such a distribution in the exciting spectrum never occurs in practice, but we may utilize our result as follows: let us choose that wave-length λ_2 at which the flux of exciting light, J_2', bears the greatest ratio to the black body flux, and let J_1' in (5) be taken to bear this same ratio to black body radiation at wave-length λ_1; then clearly the value of F_1' given by (5) sets an upper limit to the intensity of fluorescent emission obtainable. For the fluorescent emission would have this value if the exciting intensity were increased until it stood in the same ratio to black

body radiation at all other wave-lengths as it does at λ_2. Substituting such a value of J_1' in (5) and letting F_1' denote the intensity of fluorescence actually obtained, we have

$$F_1' \leqq \beta_1 \frac{J_1}{J_2} J_2', \tag{6}$$

where J_1 and J_2 refer to black body radiation at λ_1 and λ_2 resp. If Planck's law holds,

$$\frac{J_1}{J_2} = \left(\frac{\lambda_2}{\lambda_1}\right)^5 e^{-\frac{1.44}{T}\left(\frac{1}{\lambda_1}-\frac{1}{\lambda_2}\right)};$$

or, taking $T = 293°$ abs. and λ_1 of the order of $5 \cdot 10^{-5}$ cm., roughly

$$\frac{J_1}{J_2} = e^{-100\left(\frac{\lambda_2-\lambda_1}{\lambda_2}\right)}$$

and therefore

$$F_1' \leqq \beta_1 e^{-100\frac{\lambda_2-\lambda_1}{\lambda_2}} J_2'. \tag{7}$$

Observational material for an exact test of (7) is lacking; but certain qualitative conclusions can be drawn. If the exciting light at the wave-length λ_2, where it differs most from black body radiation, is of shorter wave-length than the fluorescence ($\lambda_2 < \lambda_1$), the exponential will be greater than unity and usually very large, yet fluorescence is at best relatively weak: thus the fluorescence absorption β_1 may easily be exceedingly small and impossible to detect, which is in harmony with the fact that fluorescent substances commonly show no unusual absorption in the region where the fluorescence is strongest. But where Stokes's law is violated ($\lambda_2 > \lambda_1$), the exponential becomes very small, and either β_1 must increase greatly or the intensity of fluorescent emission per unit volume must become very small, and in either case the fluorescence would be difficult to observe. Stokes's law should therefore in practice be nearly true; and as a matter of fact violations of it have not been observed for a value of $(\lambda_2 - \lambda_1)/\lambda_2$ much exceeding .03, for which the exponential in (7) becomes .034. But even over this restricted range the fluorescence can hardly be of visible intensity unless β_1 is of appreciable magnitude; and it is noteworthy that in solids and liquids, at least, violations of Stokes's law seem to be observable only where the fluorescence band is known to overlap an absorption band.

Apparently no further results can be obtained with complete rigor. But it is a characteristic feature of thermodynamics that further conclusions of great interest can often be obtained by adding certain more or less plausible assumptions; in other words, it is often possible to find

a special set of assumptions which taken together are incompatible with the second law; and while thermodynamics does not tell us which assumption is the faulty one, yet we can often decide this point with good probability on other grounds. An instance of this is afforded by Stokes's law, which can be deduced theoretically only if the fluorescence absorption is ignored.

Similarly, absorption of the *exciting* light can probably not be inferred with rigor from thermodynamical considerations—the fluorescent energy might be derived from the heat energy of the substance. But the additional assumptions required in this case are so plausible and the general likelihood of the conclusion is so strong that the occurrence of such an absorption is highly probable. Its existence will accordingly be assumed in the second part of the paper.

II.

The general argument thus leaves undecided the double question, what is the source of the fluorescent energy, and what becomes of that part of the absorbed energy which corresponds to the fluorescence and is determined by the coefficient β; further progress is possible only on the basis of special hypotheses. We shall accordingly assume, first, that thermal emission and fluorescence are thermodynamically independent so that the thermal emission and its equilibrating absorption, determined by the coefficient α, may be left out of account without affecting our conclusions touching the fluorescence; and, second, that the energy of fluorescence is under all circumstances derived entirely from the energy of the exciting light. The latter assumption seems especially plausible in view of the fact that the fluorescent process leaves (by the general hypothesis underlying the present paper) no permanent change in the substance and should therefore be accompanied by no net heat change; the immediate action of the exciting light, if it consists in a chemical transformation or in the liberation of electrons, may well be accompanied by a reversible heat change, but the latter should be exactly reversed during the occurrence of recombination with the emission of fluorescent light.

These two assumptions lead at once to the conclusion that the energy absorbed from each monochromatic component of the exciting light in consequence of the fluorescence absorption β is equal to the energy of fluorescent emission excited by that component. For when fluorescence is excited by an isolated monochromatic beam the absorption cannot be less than the emission, there being by hypothesis no other source of energy available for the latter. But then, if the absorption exceeded the

excited emission for certain wave-lengths, the absorption from full radiation would exceed full fluorescence, whereas for equilibrium (since we may ignore thermal absorption and emission) these two quantities are equal.

Expressing the conclusion just stated in symbols, we have, for any spectral intensity of flux J_1' of the exciting light,

$$\beta_1 J_1' = \int_0^\infty f_{21} J_1' d\lambda_2,$$

where f_{21} denotes as before the intensity of fluorescent emission at λ_2 excited in unit volume by unit flux at λ_1, so that the right-hand member denotes the total fluorescent emission per unit volume and per unit of wave-length of the exciting light.

Hence

$$\beta_1 = \int_0^\infty f_{21} d\lambda_2, \tag{8}$$

which states simply that at any wave-length the coefficient of fluorescence absorption is equal to what we may conveniently call the "exciting power," viz., the total fluorescent emission per unit volume excited by unit flux of that wave-length. This gives us a definite indication of the magnitude of the fluorescence absorption which we were not able to obtain without the aid of our special hypotheses. Since in practical cases the exciting power is always very small, the same will be true of the fluorescence absorption.

We may now combine this result with (1) and (4), obtaining

$$\int_0^\infty f_{12} J_2 d\lambda_2 = J_1 \int_0^\infty f_{21} d\lambda_2, \tag{9}$$

where J_1 and J_2 refer now to black-body radiation. This may be regarded as an integral equation for the determination of the coefficient of fluorescence $f(\lambda_1, \lambda_2)$. The range of possible solutions is too broad to allow of any rigorous conclusions, but a solution whose simplicity commends it as physically probable is:

$$f_{12} J_2 = f_{21} J_1. \tag{10}$$

If we may assume that fluorescence is proportional to the intensity of excitation, so that f is independent of the latter, then this equation would assert that the spectral intensity of fluorescence at λ_1 excited by unit flux of wave-length λ_2 bears to the reverse intensity at λ_2 excited by unit flux at λ_1 the same ratio as the intensities in the black body spectrum

at λ_1 and λ_2 resp. If this conclusion is correct, the reason for the approximate validity of Stokes's law becomes very evident.

Equation (10), assuming proportionality, lends itself readily to an experimental test even in the case of a line spectrum. Let two narrow wave-length intervals be selected, $\Delta\lambda_1$ and $\Delta\lambda_2$, each including one or more lines, and let the specimen be illuminated with portions of a continuous spectrum confined in turn to each of the chosen intervals but having in both cases the same uniform spectral intensity of flux, J'. Then the total fluorescent energy in the interval $\Delta\lambda_2$ emitted per unit volume when the exciting light lies in $\Delta\lambda_1$ will be

$$F_2' = J' \int_{\Delta\lambda_1} \int_{\Delta\lambda_2} f_{21} d\lambda_1 d\lambda_2,$$

while that in $\Delta\lambda_1$ when $\Delta\lambda_2$ is excited will be

$$F_1' = J' \int_{\Delta\lambda_1} \int_{\Delta\lambda_2} f_{12} d\lambda_1 d\lambda_2.$$

Now throughout these small intervals the black body intensity J_1 and J_2 in equation (10) may be supposed constant, so that we can substitute in the second integral

$$f_{12} = \frac{J_1}{J_2} f_{21}$$

and treat the ratio J_1/J_2 as a constant. We then obtain

$$\frac{F_1'}{F_2'} = \frac{J_1}{J_2}; \tag{11}$$

that is, the *total* fluorescent emissions excited in these two intervals of wave-length under the conditions stated are proportional to the corresponding intensities in the black-body spectrum. This conclusion could easily be tested by using a mechanical photometer such as a photoelectric cell.

Further theoretical progress is, however, possible, without loss of rigor, if we assume, as has in certain cases been found to be true, that the distribution of intensity within a fluorescence band is independent of the wave-length of excitation. We may then write

$$f(\lambda_1, \lambda_2) = \zeta(\lambda_1)\varphi(\lambda_2), \tag{12}$$

where $\varphi(\lambda_2)$ is the "exciting power" or total fluorescent emission excited in unit volume by unit flux at λ_2, while $\zeta(\lambda_1)d\lambda_1$ is the fraction of this

emission included within $d\lambda_1$ at λ_1. (9) then takes the form

$$\zeta(\lambda_1)\int_0^\infty \varphi(\lambda_2)J(\lambda_2)d\lambda_2 = \varphi(\lambda_1)J(\lambda_1)\int_0^\infty \zeta(\lambda_2)d\lambda_2.$$

This may be written

$$\zeta(\lambda_1) = C\varphi(\lambda_1)J(\lambda_1),$$

where C is a fixed number; substitution shows that the value of C may be assigned artbirarily, so that this is the general solution of the integral equation. But in the physical case by definition

$$\int_0^\infty \zeta(\lambda_1)d\lambda_1 = 1,$$

whence

$$1 = C\int_0^\infty \varphi(\lambda_1)J(\lambda_1)d\lambda_1 = C\Phi,$$

where Φ stands for the last integral and represents the total full fluorescent emission per unit volume irrespective of wave-length.

Hence

$$\zeta_1 = \frac{1}{\Phi}\varphi_1 J_1 \tag{13}$$

and

$$f_{12} = \frac{1}{\Phi}\varphi_1\varphi_2 J_1. \tag{14}$$

In words, (13) states that *the intensity at any point in a homogeneous fluorescence band is proportional to the intensity in the black body spectrum at that point multiplied by the power of light of that wave-length to excite the band.*

All of these results hold, strictly, only for excitation by radiation of the same temperature as the fluorescing substance. In seeking an extension to other temperatures there appear to be two plausible paths along which we may proceed.

If the fluorescent process consists in the ejection of electrons from the atom with subsequent recombination accompanied by the emission of light, then, by analogy with the photo-electric effect, we should expect the rate of ejection of electrons and hence also the rate of fluorescent emission to be proportional to the exciting intensity, while the form of the spectrum should be independent of it; ζ and φ will then depend only on the temperature of the substance and J is to be taken for that temperature.

If, on the other hand, the fluorescence is due to some kind of resonance

within the atom, then it seems quite possible that equations (10), (13) and (14) will hold when J is taken for the temperature of the exciting light, the temperature of the substance affecting the phenomenon only indirectly by altering the properties of the resonators. But then a change in the temperature of the exciting light will alter J, so that if (10) holds, f must change with a change of temperature; while if (13) and (14) hold, then either ζ or φ, or both, must change with a change of temperature, since the change in J does not consist in multiplication by a constant factor. Now a change in the *intensity* of the exciting light may or may not change its temperature: if the intensity is varied by moving the source parallel to the beam the temperature remains unaltered; while if the intensity is altered by interposing a diffusing screen the temperature will be lowered. Accordingly, in the former case we should expect the coefficient f to remain constant, *i. e.*, proportionality should hold for all wave-lengths of excitation and emission; while in the latter case f would, in general, be altered and proportionality between excitation and emission could not hold for all wave-lengths, the change occurring either in ζ or in φ, or in both, in the simple case characterized by (12).

It is interesting to note that if J obeyed the Rayleigh-Lorentz law its *form* would *not* change with a change of temperature and this breakdown of proportionality would not be required by our equations. If the latter really occurs, therefore, it will probably find its ultimate explanation in the factors which lead to the failure of equipartition, whatever these may turn out to be.

Let us in conclusion turn to the comparison of the last results obtained with observation. The fluorescence of gases exhibits peculiarities strongly suggestive of resonance, but unfortunately no quantitative data seem here to be available. On the other hand, in liquids and solids the close connection usually found between fluorescence and phosphorescence suggests the first alternative described above, viz., the production of some intermediate change such as ionization or a chemical change, so that the fluorescence ought to be related to the temperature of the substance rather than to that of the exciting light.

Two substances which possess an isolated unitary band and which should therefore, if the theory developed here is correct, obey equation (13), are eosin and resorufin, and fortunately the necessary data are available in a paper by Nichols and Merritt[1] in the PHYSICAL REVIEW. In their Table I. they give what they call the "specific exciting power" for eosin, meaning the excitation per unit of absorbed energy; hence this

[1] E. L. Nichols and E. Merritt, PHYS. REV., XXXI., p. 381, 1910.

quantity multiplied by the coefficient of absorption, given in the same table, gives values of φ, which is here called the exciting power and represents the excitation per unit of light flux. For resorufin, numbers proportional to φ are obtained by multiplying the ordinates of the crosses and circles in their Fig. (93) by the corresponding ordinates of the absorption curve A in the same figure.

The experimental values of φ thus obtained are shown by the circles on the annexed plots (Figs. 1 and 2). The distribution in the fluorescence spectrum,[1] which is known to be independent of the exciting light, is shown by the curves marked ζ. We may suppose the temperature of the specimens to have been about 20° C.; the black body curve for this temperature is shown by the curves marked J (the slight variation of the refractive index with wave-length is left out of account.) Finally, the theoretical values of φ given by equation (13) in the form

$$\varphi = k\frac{\zeta}{J}$$

are shown by the curves marked φ, the single constant k being adjusted for a good fit. [By (8) above, $\varphi = \beta$, so that the latter curve represents also the coefficient of fluorescence absorption.]

The agreement between observed and calculated values of φ is about as good as could be expected under the circumstances. The slope of the theoretical curve over its central portion is almost exactly right and it shows indications of a maximum in the right place; it fails chiefly

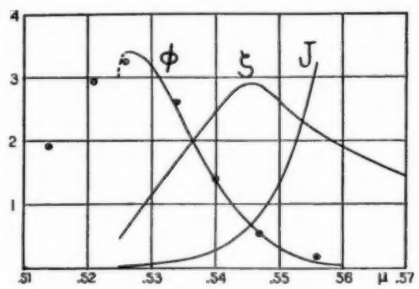


Fig. 1.
Eosin.

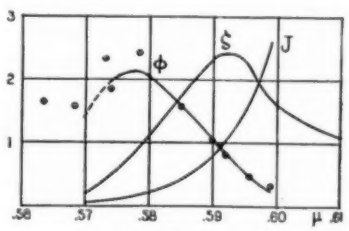


Fig. 2.
Resorufin.

at the ends, where either the fluorescence or the exciting power is small and therefore not known with certainty. A change of 10 per cent. in the slope would result from a change of 30° in the temperature or of 0.03 μ in the wave-length employed in calculating J. The final test of the theory must wait however until the region in which both quantities are experimentally known shall have been considerably extended.

[1] E. L. Nichols and E. Merritt, PHYS. REV., XXX., p. 345, 1910.

It is a pleasure to acknowledge a debt to Professor E. Merritt for his obliging assistance as critic during the development of this paper.

SUMMARY.

By applying thermodynamics to fluorescent substances a relationship is deduced between the coefficient of fluorescence absorption, the intensity of fluorescence and the intensity of black body radiation.

Adding the assumptions that fluorescence and thermal radiation are thermodynamically independent and that the energy of fluorescence is derived from that of the exciting light, it is concluded that in the case of an isolated unitary band

$$\zeta = k\varphi J,$$

where ζ = relative intensity in the fluorescence spectrum, φ = exciting power, and J = intensity in the black body spectrum for the temperature of the substance, all being taken for the same wave-length; and this equation appears to be confirmed by observed data.

CORNELL UNIVERSITY,
March, 1917.

KATHODO-FLUORESCENCE OF CRYSTALS.

By Thomas B. Brown.

Part I.—A Quantitative Investigation of the Kathodo-Fluorescence of Willemite, Kunzite and Soda Glass. (A description of the results obtained by J. A. Veazey.)

Part II.—A Further Investigation of Willemite by the writer.

Introduction.

THE intensity of the fluorescence excited by the impact of kathode rays upon a fluorescent substance depends, for a given substance at a constant temperature, upon the velocity of the rays, and upon their rate of impact. To a lesser degree it may be affected by other factors as yet undetermined.

The experimental study naturally divides into two parts:

1. A determination of the relation between the intensity of the fluorescent light L and the kathode ray current I at constant discharge potentials.

2. A determination of the relation between L and the discharge potential V at constant current values.

The earliest investigation was made by Lenard.[1] Lenard had only a secondary interest in the phenomenon, as a means of detection of kathode rays. He investigated several substances, making on each substance only a few observations through the limited range he was interested in; from the results he postulated the relation

$$L = CI(V - V_0),$$

where V_0 is a minimum potential *below which no fluorescence can occur*. No experimental proof of the existence of this minimum is given; and it seems, in the light of later investigation, an unjustifiable extrapolation.

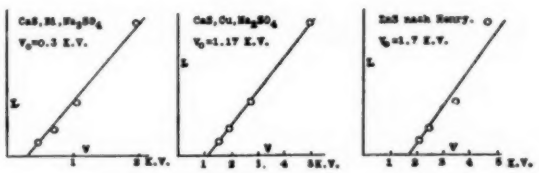


Fig. 1.

Plotted from data of Lenard. The lines drawn represent the equation he gives for them:

$$L = CI(V - V_0).$$

[1] P. Lenard, Ann. d. Phys., 12, 1903, pp. 449–490.

The points plotted in Fig. 1 represent his observations on several substances, and the straight lines drawn, his interpretation of them.

The next observer in this field was Leithäuser,[1] who likewise wished to use the phenomenon as a means of detecting kathode rays. Working with calcium-sulphide, he found an exact proportionality between L and I at constant V, but found the non-linear relation between L and V at constant I which is given by Fig. 2, plotted from his data. It is to be noted that, curiously enough, this curve, if extended backward, would cut the *intensity* axis!

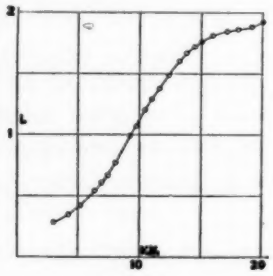


Fig. 2.

Intensity-potential curve obtained by Leithäuser for CaS.

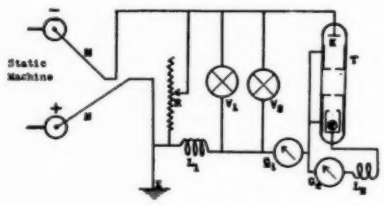


Fig. 3.

Diagram of connections.

Directly following a brief preliminary investigation by Nichols and Merritt,[2] in connection with a study of the spectrum of kathodo-fluorescence as influenced by the velocity of the exciting rays, J. A. Veazey took up, at their suggestion, an extended investigation of the problem. His untimely death in the summer of 1912 cut his work short. To the present writer, whose good fortune it had been to act as Veazey's assistant the previous year, fell not only the continuance of the work, but also the editing for publication of Veazey's work. This paper is accordingly in two parts, as indicated in the heading above.

PART I.—THE KATHODO-FLUORESCENCE OF WILLEMITE, KUNZITE AND SODA GLASS. (DESCRIBING THE MEASUREMENTS BY J. A. VEAZEY.)

After extended preliminary experiments which led to the elimination of several important sources of error, the apparatus was finally arranged as shown in diagram in Fig. 3.

Current is supplied to the discharge tube T through the high-tension reversing switch MN from the large Holtz machine H. An alcohol rheostat R in shunt with the Holtz machine regulates the current through the tube, and Kelvin electrostatic voltmeters V_1 and V_2, having over-

[1] G. E. Leithäuser, Ann. d. Phys., 15, 1904, pp. 283–306.

[2] E. L. Nichols and E. Merritt, PHYS. REV., 28, 1909, pp. 349–360.

lapping ranges, measure the potential difference across the tube. A sensitive Sullivan galvanometer G_2 measures the current carried to the crystal by the kathode rays, and the galvanometer G_1 measures the total current passing through the tube. Ironless inductances L_1 and L_2 are inserted to prevent oscillations.

The tube is shown in section in Fig. 4. Kathode rays projected from the kathode K along the axis of the tube strike the crystal W, causing fluorescence. The cylindrical box anodes C_1 and C_2 shield off all but the central portion of the bundle of kathode rays, and receive all the current passing through the tube except that carried by this central portion of the rays. For reasons explained later, the lower box C_2 may , when desired, be maintained at a potential of -55 volts with respect to the inner box M, by throwing over the switch S. The crystal W is surrounded by the aluminum box M, whose purpose it is to receive the current carried to the crystal by the kathode rays and to conduct it to the galvanometer G_2.

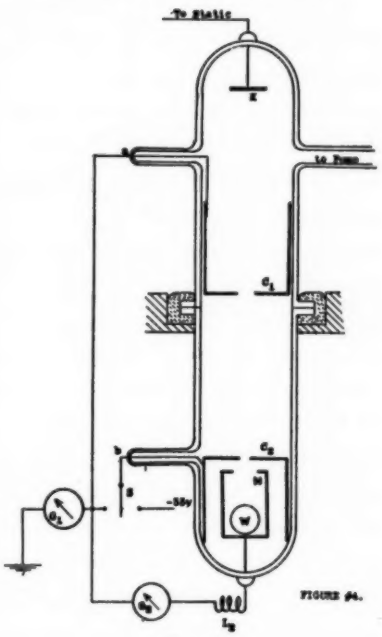


Fig. 4.

The tube is evacuated by a Pfeiffer-Wetzlar rotary mercury pump and a Fleuss oil pump in series. The vacuum system was so tightly closed and so free from vapor that pumping at intervals sufficed to maintain any desired potential difference across the tube.

Through holes in the sides of the boxes C_2 and M photometric measurements are made. The photometer used was designed especially for the work. A Lummer-Brodhun cube matches the illumination of two transmission-diffusion screens; one of these is illuminated by the fluorescence of the crystal, the other by a constant comparison source. By a suitable variation of these calibrated screens, any range of visible fluorescence may be measured. The small central portion of a large acetylene flame as seen through a circular hole in a diaphragm placed directly in front of it and covered with a suitably colored glass or liquid screen to give a visual color match with the fluorescent light, is used as the comparison source. The gas pressure was kept constant, and the outline of the flame, as observed in a flame gauge, remained constant. The

distance from the crystal to its diffusion screen is fixed, while the comparison source is movable along a photometer bar. Since Nichols and Merritt[1] have shown that the spectral distribution for the substances examined is independent of the electrical conditions of the discharge (or indeed, of the method of excitation), ordinary photometric measurement is sufficient.

It was found upon trial with willemite that, for potentials below 1.5 K.V., with the box C_2 earthed, the galvanometer G_2 reads zero, and no light is given off by the crystal; but as the potential is raised, it began to deflect when the crystal began to fluoresce. At any discharge potential, a deflecting magnetic field reduced the galvanometer reading to zero at the same time as it stopped all fluorescence of the crystal. These tests seem to indicate that the current represented by the galvanometer reading is exclusively kathode ray current. They do not prove, however, that all of the impinging electrons contribute to the current read by this galvanometer; since the rays suffer reflection, a part of the reflected rays may escape through the openings in the box M and carry their charges to the cylinder C_2. But if the loss by reflection is independent of the potential and of the gas pressure, the data will still give the true relation between the intensity of the fluorescence, the current, and the potential. L. Austin and H. Starke[2] find the reflecting power of *metals* for kathode rays at normal incidence independent of the gas pressure and the potential within the limits of 3 to 30 K.V. No statement of work covering the case at hand has been found. Here the crystal is non-conducting, and the rays are incident at an angle of forty-five degrees. It will be assumed, however, that the reflecting power in this case also is independent of the potential and gas pressure.

Experiments with Willemite

The first crystal examined was a specimen of willemite (zinc orthosilicate) having an area of about one square centimeter ground smooth. A circular area about 0.80 cm. in diameter was bombarded by the kathode rays.

Curve 1, Fig. 5, represents data taken at the constant potential of 3.50 K.V., with the cylindrical box C_2 earthed. Curve 2 was taken with this box charged to a small negative potential ($-$ 55 volts). These results seem to indicate that with C_2 earthed not all of the reflected electrons are caught by the box M; while with C_2 at a small negative potential, more if not all of the electrons are caught and their charge

[1] E. L. Nichols and E. Merritt, PHYS. REV., 28, 1909, pp. 349–360.

[2] L. Austin and H. Starke, Ann. d. Phys., IX., p. 271, 1902.

measured by the galvanometer G_2. For all subsequent observations C_2 was kept at the potential of $-$ 55 volts.

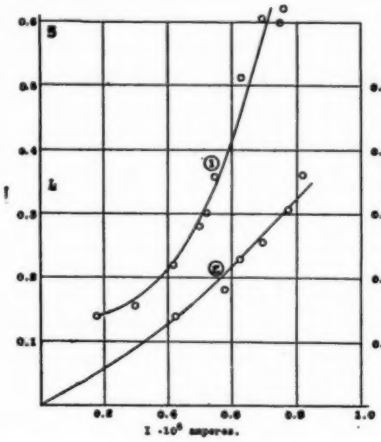


Fig. 5.

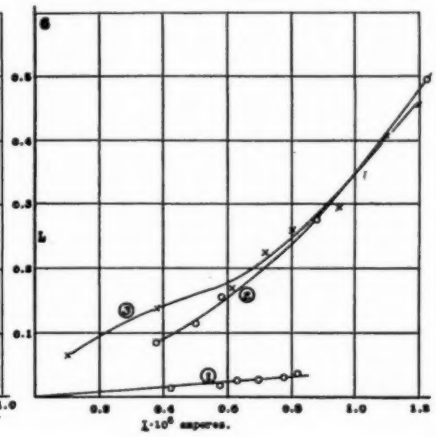


Fig. 6.

Potential constant at 3.50 K.V.

Curve 1. Cylinder C_2 grounded.

Curve 2. Cylinder C_2 at potential of $-$ 55 volts.

Potential constant at 3.50 K.V.

Curve 1. Taken March 4th. Pressure maintained low previously.

Curve 2. March 4th. After admission of air and reëxhaustion.

Curve 3. March 8th. Same conditions as No. 2.

Fig. 6 shows the effect of admitting fresh air into the tube. Curve 1 was taken after low gas pressures had been maintained for several days' use of the tube. Curve 2 was taken the same day after admitting air to the tube to atmospheric pressure, and reëxhausting. Curve 3 was taken a few days later, conditions similar to those of 2 having been maintained approximately in the interim. As a result of the admission of fresh air it is to be noticed that (*a*) for a given kathode ray current there is a marked increase of the intensity of fluorescence, and (*b*) with the same external circuit conditions, a much greater kathode ray current may be obtained. The first of these results may be due to some change in the surface condition of the crystal; perhaps to its oxidation by the freshly admitted air. The subsequent bombardment of the crystal, together with the removal of the gases of decomposition by pumping, may again reduce the surface. Villard[1] found in his experiments that the portion of an oxidized copper plate exposed to the action of kathode rays became bright, and he considered this a reduction of the surface due to the bombardment.

[1] J. J. Thompson, Cond. of Elec. through Gases, p. 496.

The second result may be explained by assuming that the walls of the tube become conducting when bombarded with kathode rays. Many observations show that after low gas pressures and high potentials have been maintained for several days, the discharge is much less concentrated along the axis of the tube; a greater portion of it being deflected toward the wall of the tube above the anode, as is shown by the increased fluorescence of the glass walls, by the lower reading of the galvanometer G_2, and by the occasional snapping of sparks from the kathode to the nearest portion of the walls. With the tube freshly exhausted, the glass walls are but slightly fluorescent, and the path of the rays, as marked out by the blue glow, is along the axis of the tube.

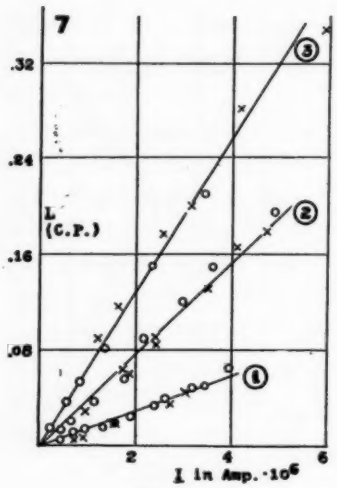


Fig. 7.

Constant potential curves for willemite, taken under conditions of maintained low pressures.

No. 1. 8.30 K.V.
No. 2. 12.20 K.V.
No. 3. 14.20 K.V.
Area bombarded, 0.5 cm.²
O Ascending values.
× Descending values.

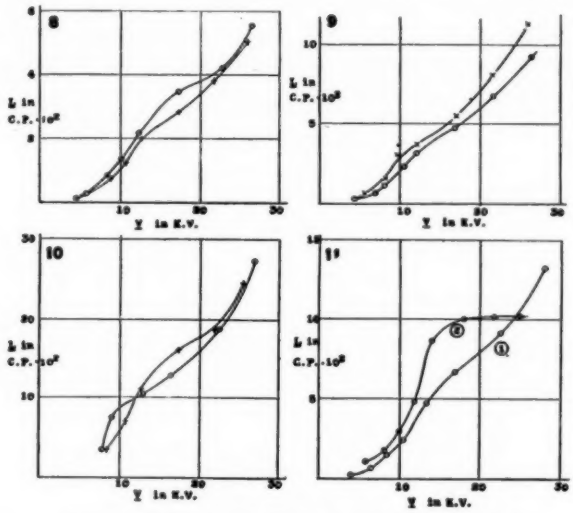
The curves shown in Fig. 7 are a part of a series of constant potential curves taken under conditions of maintained low pressures. These, as well as the others not shown, are all straight lines within the limits of experimental error, and show a direct proportionality between the intensity of fluorescence and the kathode-ray current. A great number of other curves, taken both before and since, likewise verify this linear relation.

This is so far in agreement with the Lenard formula

$$L = CI(V - V_0).$$

In order that complete agreement obtain, data taken at constant current should plot as straight lines for the intensity-potential relation, with an intercept on the potential axis equal to V_0. Figs. 8, 9, 10, 11 represent the data obtained for the constant current values indicated. None of these curves are straight lines, and all of them show decided hysteresis effects for increasing and decreasing potentials. These curves might possibly be considered straight lines with the superimposed effects of changes of temperature, of change of reflecting power with change of potential, and of fatigue and hysteresis. The lowest potential at which fluorescence of willemite could be detected was 1.40 K.V. The curves do not approach the axis close enough to determine an intercept accurately.

Curve 2, Fig. 11, illustrates another method of obtaining the relation between intensity and potential at constant current. It was plotted from the series of constant potential curves, a part of which are shown



CONSTANT CURRENT CURVES FOR WILLEMITE.

Fig. 8.

Current value of $0.65 \cdot 10^{6}$ Amp.

Fig. 9.

Current value of $1.30 \cdot 10$ Amp.

Fig. 10.

Current value of $3.20 \cdot 10$ Amp.

Figs. 8, 9, and 10, illustrate different types of hysteresis.

Fig. 11.

Current value of $1.30 \cdot 10$ Amp.

Curve 1 was taken directly.

Curve 2 was obtained from the series of constant potential curves of which the curves in Fig. 7 are a part.

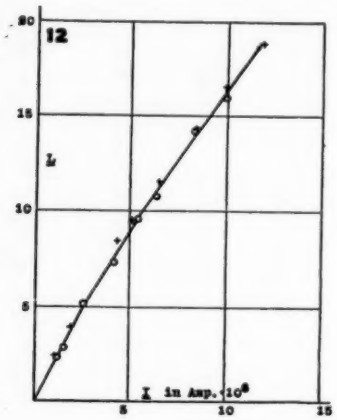
in Fig. 7, using values read from those curves corresponding to the current of $1.3 \cdot 10^{-6}$ amperes. It is to be recalled that this series of constant potential curves was taken under conditions of maintained low gas pressures, so that the bending of the upper part of this curve toward the horizontal may be due to a slow deterioration of the fluorescent power with time.

Experiments with Kunzite.

A crystal of kunzite (a variety of spodumene, $LiAl(SiO_3)_2$) was next examined. Kunzite is fluorescent only under spark or kathode ray

excitation, with an amber or reddish yellow fluorescence. This crystal was less permanent under kathode ray bombardment than willemite, giving off decomposition vapors much more rapidly, and exhibiting other fatigue or decomposition phenomena to be described later.

The curves for kunzite are very similar to those for willemite in form, but the relative intensity is considerably less. The constant potential curves, of which Fig. 12 is an example, all show a good proportionality



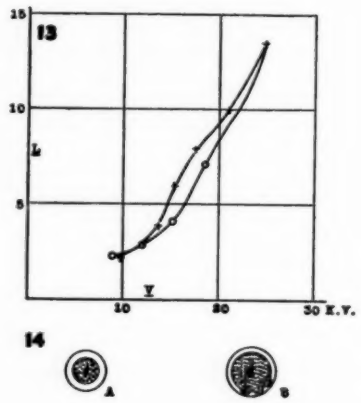


Fig. 12.

Kunzite. Potential, 17.15 K.V. Area bombarded, 0.2 cm.²

Fig. 13.

Kunzite. Current, $3.88 \cdot 10^{-6}$ Amp.

Fig. 14.

Kunzite. Appearance of bombarded area. *A*, Low potentials. *B*, High potentials.

between the intensity of fluorescence and the current; while the constant current curves, of which Fig. 13 is an example, are non-linear, much resembling the corresponding ones for willemite, and show a considerable hysteresis between the ascending and descending values.

Direct observation of the fluorescing crystal discovered that the fluorescing area was not uniformly bright, but appeared as a luminous ring surrounding a darker central area, with a very dark spot near its center. At low potentials this ring grew to greater diameter, but became narrower, and scallops appeared, extending into the ring from the center. Fig. 14 illustrates this. These phenomena lead to the supposition that the kathode ray bundle incident upon the crystal is not homogeneous, but is more or less hollow, depending upon the potential. Such a hollowness has been reported by Swinton.[1]

[1] C. Swinton, Proc. Roy. Soc., LXI., p. 79, 1897.

Examination after removal from the tube found the surface of the crystal to be discolored where it had suffered bombardment; there being a dark spot near the center surrounded by a discolored ring. Several hours' heating at several hundred degrees Centigrade completely removed this discoloration, together with the natural lilac color of the crystal, so that it now appeared as clear glass. The fluorescent properties were but little changed, as Fig. 15, taken after heating, shows. The noticeable change is the absence of any hysteresis effect. For these observations the distribution of the rays was rendered more uniform by placing a plate of aluminum drilled full of fine holes over the opening in the cylinder C_2.

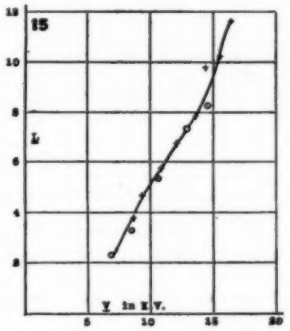


Fig. 15.

Kunzite, after heating. Current value, $0.634 \cdot 10^{-6}$ Amp.

Experiments with Glass. (*Soda glass of German manufacture.*)

A piece of glass taken from a broken discharge tube was next examined. The fluorescence is a greenish color, and much weaker than that of either of the substances previously examined. The results obtained, shown in Figs. 16 and 17, indicate the same general relation between the variables

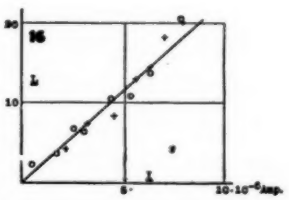


Fig. 16.

Glass. Potential, 19.1 K.V.

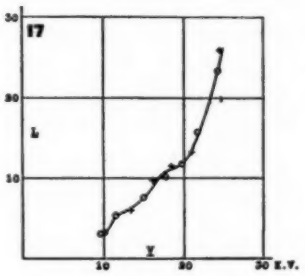


Fig. 17.

Glass. Current, $3.88 \cdot 10^{-6}$ Amp. Area bombarded, 0.2 cm.^{2}

as holds for the other substances: a direct proportionality between intensity and current at constant potentials, and a non-linear relation between intensity and potential at constant currents. There is little if any hysteresis. Direct observation discovered the same phenomena of non-uniform luminosity as observed for kunzite, when the opening in the top of the cylinder C_2 was uncovered.

Conclusions.

1. For potentials not too small, the constant potential curves obtained for willemite and kunzite show a direct proportionality between the intensity of fluorescence and the kathode ray current, and so far verify the relation postulated by Lenard

$$L = CI(V - V_0).$$

The single curve for glass agrees approximately.

2. If precautions are taken to prevent loss of charge by reflection, the curves obtained for willemite and kunzite for small discharge potentials likewise show this proportionality; except that, for the same potential, a much steeper line is obtained in a freshly exhausted tube than is obtained after the vacuum has been maintained at a low gas pressure, and discharge passed at a high potential, for some time previously.

3. The constant current curves for willemite, kunzite, glass, and the heat-treated kunzite, do not agree with the Lenard formula, although they come closer to it than do the results of Leithäuser. The constant-current curves for willemite and native kunzite show marked hysteresis effects, while the glass and the colorless (heat treated) kunzite do not.

4. The crookedness of the constant current curves may be due to the effect of changes of temperature upon the fluorescent power of the crystal, or to changes of the reflecting power of the crystal, with changes of potential.

Some means must be provided to insure these conditions are constant before the exact relation between the intensity of fluorescence and discharge potential can be found.

PART II.—A FURTHER INVESTIGATION OF WILLEMITE.

If L is known to be a function of I and V, and it is found that for V constant, L is directly proportional to I, then it follows that the ratio L/I is a function of V alone. The results of all investigators agree that, at a constant discharge potential V, the intensity of fluorescence L is directly proportional to the kathode-ray current I. Particularly conclusive evidence seem the abundance of curves verifying this relation obtained by Veazey. This continuation of the work is concerned with, first, checking the apparatus used by determining whether or not it will give this same relation between L and I at constant potential, and then determining the form of the relation between L/I and V.

Willemite was chosen for further investigation as typical of these substances and also as being the most brilliantiy fluorescent of them, and the most stable under the kathode-ray bombardment. The speci-

men was used in powdered form, the crystals being chipped away from the quartz with which they occurred, powdered, and then heated to redness to drive off any volatile or gaseous impurities present. After heating the color was almost white, but the fluorescent properties remained unchanged. This specimen never gave evidence of the hysteresis and tiring effects found by Veazey in his specimen; and this fact is probably due to the preliminary heating.

It is to be recalled that for these substances at room temperature the spectral distribution is the same for all discharge potentials.[1] The effect of temperature upon the spectral distribution has been investigated by Nichols,[2] and is found to be inappreciable in the range of ordinary room temperatures.

The discharge tube used is shown in vertical section in Fig. 18. This tube is similar to the one used by Veazey, but much larger. The upper part of the tube *A* is about 13 cm. in diameter and stands 24 cm. high. The height over all is about 55 cm. and the volume approximately 3.3 liters. The kathode *K* is 2.7 cm. in diameter. The anode, the two concentric cylindrical aluminum boxes *M* and *N*, occupies a major portion of the tube. The distance between the top of the box *M* and the kathode is 2.4 cm. The outer box *M* is earthed and receives all the discharge except that part carried by the central portion of the kathode stream which enters the inner box *N* through the circular openings *a*, *b*, and *c*, and bombards the fluorescent powder at *d*. *N* is insulated from *M* by the glass plate which supports it, and the charge carried to *d* by the rays is conducted through *C* to the galvanometer *G* and thence to the earth. The area of powder surface bombarded is about one centimeter in diameter. The upper opening *a* was covered with a multi-perforated plate, as this was found desirable by Veazey. A sixty-degree prism *o*, sheathed with aluminum except for openings as shown, reflects the fluorescent light through holes in the sides of the boxes *M* and *N*, and

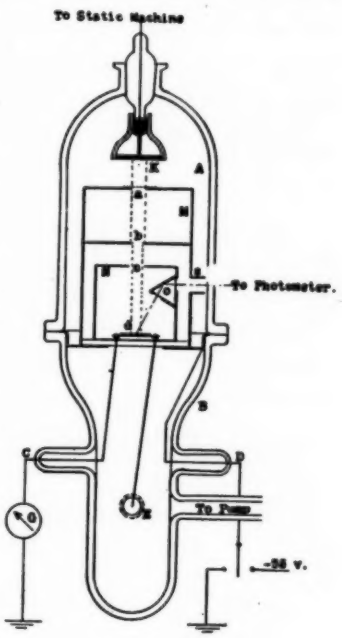


Fig. 18.
Vertical section of discharge tube.

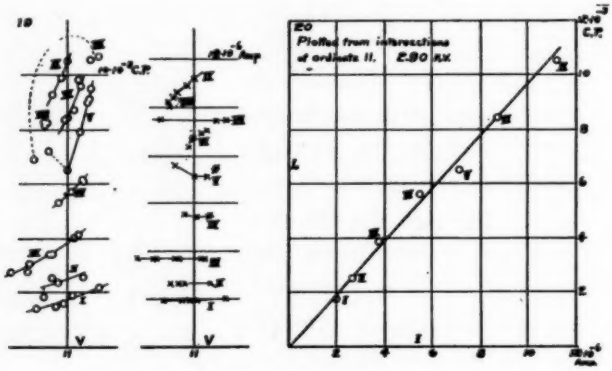
[1] E. L. Nichols and E. Merritt, PHYS. REV., 28, 1909, p. 349–360.
[2] E. L. Nichols, Proc. Amer. Phil. Soc., 196, 1910, pp. 267–280.

the tube s (placed here to prevent any stray discharge reaching N), and thence into the photometer. In this form of anode the possibility of loss of charge due to reflection is very much smaller than in the form used by Veazey, and it was unnecessary to give the outer anode a negative potential to prevent loss.

The pumping system is the same as that used by Veazey, and the electrical system likewise (see Fig. 3), except for a few minor connections, and the addition of a third static voltmeter, built by the author, to cover a lower range of potentials than the others. All permanent connections are soldered. The voltmeters were calibrated and checked against an attracted disc electrometer. The photometer used is a modified form of the one used by Veazey, with an entirely new set of calibrated comparison screens. By means of a contrast photometer comparison was made with a laboratory standard, so that the intensity values are given in approximate visual candle power.

First to be considered is the relation between the intensity of fluorescence L and the kathode ray current I at constant potentials; *i. e.* testing for this apparatus the relation $L = kI$ at constant potential, where k is a function of the potential V.

Figs. 19 and 20 show the way in which the results were plotted. Since



Figs. 19 and 20.

Method of plotting intensity-current curves.

in most cases it was difficult to hold the potential absolutely constant, and since in the same cases the change of L for a small change of V is relatively great, readings were made of a series of corresponding values of L, V, and I in the neighborhood of the desired potential; this data is plotted as in Fig. 19. Then by interpolation from these curves corresponding values of L and I at a constant potential are obtained and plotted as in Fig. 20. Fig. 21 shows the collection of curves obtained

to show the relation between L and I at constant potentials; they are all straight lines within the limits of experimental error. They cover

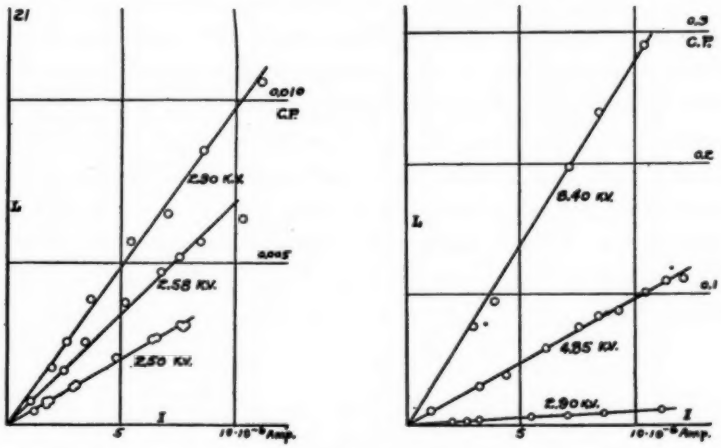


Fig. 21.

Intensity-current curves for different potentials.

fairly well the range of potentials investigated hereafter, and are considered a satisfactory agreement with the relation $L = kI$ at constant potential, which has already been pretty exactly verified by Veazey and others.

Having established the direct proportionality between L and I at constant V, *i. e.*, the relation $L = F(V)I$, it is now possible to proceed to investigate the form of the relation $F(V)$ between L/I and V. Typical results of this investigation are shown in Figs. 22, 23, and 24. Because of the great range of intensities, it was necessary to plot the results

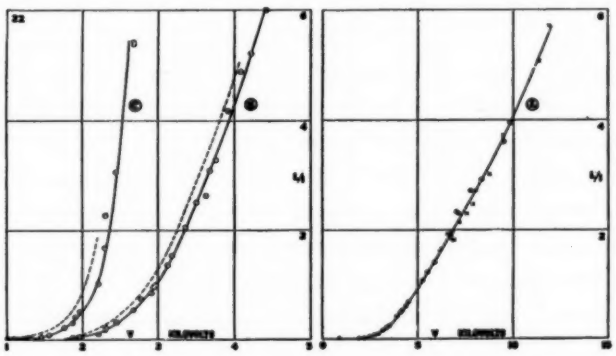


Fig. 22.

April 1. To read the values of L/I in candle power per ampere, multiply the ordinates of curve A by 10^4; of curve B by 10^3; and of curve C by 10^2. O indicates increasing values; ×, decreasing values.

of a single run (often around a hundred observations) on two sheets, and to three different scales of intensities. The results as represented by these curves are in general agreement with the results obtained by Veazey, and with those obtained by Leithäuser, with the exception pointed out heretofore. In addition, in the present work, successive observations have been made much closer together than in any previous work, and the results present a greater degree of uniformity and extend the investigation to a region of much lower potentials. The results are not in agreement with the conclusions of Lenard *i. e.*, that the relation would be a linear one, with a minimum potential existing below which no fluorescence could occur, but seem to be in good agreement with his data. Comparing Figs. 1 and 23, Curve *A*: It is easy to see how Lenard, having

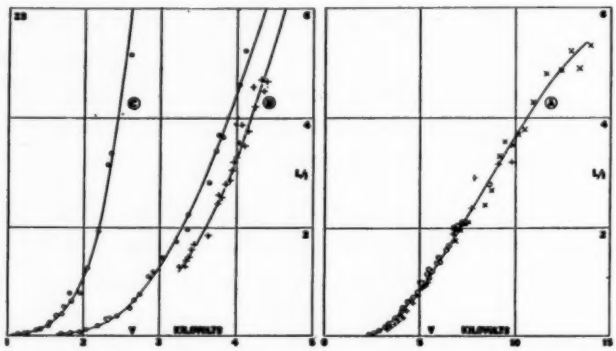


Fig. 23.

April 7. Values of L/I are read as indicated under Fig. 22. O indicates ascending values, and ×, descending values, taken in the morning. + indicates ascending values taken in the afternoon.

only a few observations in a region of potentials corresponding to the nearly straight portion of Fig. 23 (between 4 and 13 K.V.) could conclude them to represent a linear relation. It is very evident from the present work that the relation is not linear. Fig. 24 shows better than the others the marked curvature at the foot of these curves. As low down as the fluorescence could be observed the curve is bending nearer and nearer towards the horizontal. There was measurable fluorescence at 0.75 K.V.; and at even lower potentials fluorescence could be detected by viewing the crystal directly. A transverse magnetic field would stop it, and at the same time bring the deflection of the galvanometer to zero, thus proving that the excitation was by the bombarding kathode electrons. However, the fluorescence for the low potentials is so faint that the results obtained below 1.00 K.V. are not accurate; especially as a small amount of light from the now luminous discharge in the top of the tube

illuminates the specimen enough to introduce between five and twenty per cent. error for observations below one kilovolt potential. Above this, the effect becomes inappreciable, since most of the luminous discharge is then driven from the tube, and its illumination becomes a negligible amount of the total brightness, which increases rapidly.

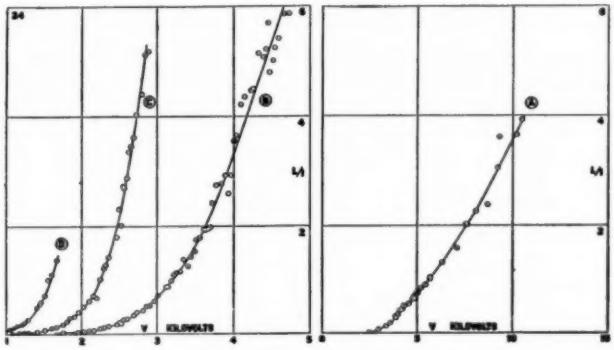


Fig. 24.

April 8. Values of L/I for curves A, B, and C are read as indicated under Fig. 22. Multiply ordinates of curve C by 10.

The lower values of L/I are undoubtedly too low; due to absorption, by the relatively greater amounts of gas present, of a part of the measured energy of the exciting electrons, and to scattering, by the same agent, of a part of the electrons, whose charges are measured, but which do not strike the crystal. There is nothing about the results obtained to indicate that, if this absorption, etc., could be eliminated, the fluorescence would not be present for all potentials down to zero potential. Certainly, if there exists a minimum potential below which no fluorescence would be produced, it is *below* the lowest value investigated here, and the data gives no evidence of its existence. If the fluorescence of such substances as willemite may be compared to the "characteristic" X-radiation of metals, computations based upon the conclusions of Duane and Hunt,[1] who found that the minimum potential for that radiation is given by the equation $eV_0 = h\nu$ (where V_0 is the minimum potential for X-radiation of frequency ν, and e and h are the electronic charge, and the Planck radiation "quanta" constant, respectively) give about 4 volts as the minimum for the middle of the fluorescent spectrum. It is doubtful if that value can be reached experimentally.

A slight change of temperature occurred during the bombardment, and was measured during some of the later runs. For example, in the case of the data of April 7, a temperature change of 19° C. occurred. This is hardly sufficient to affect the phenomena.

[1] W. Duane and F. L. Hunt, PHYS. Rev., N.S., VI., Aug., 1915, p. 166.

The results of the different runs, when compared (Fig. 25), instead of coinciding, as might have been reasonably expected, scatter considerably;

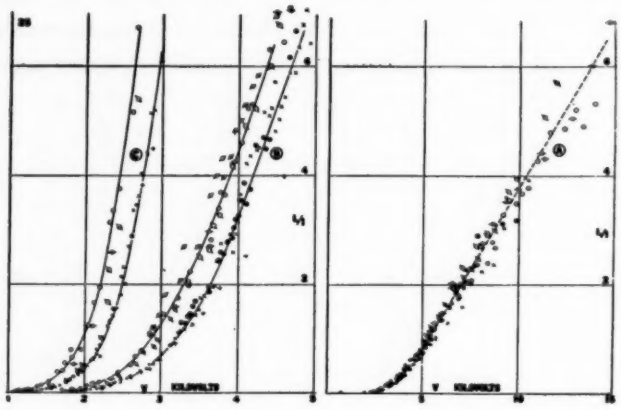


Fig. 25.

Combined results. Values of L/I are read as indicated under Fig. 22. Different runs are indicated as follows: January 21 +, February 10 ○, March 18 -○-, April 1 , April 7 ⊙ ⊗ and April 8 ×.

but in general, they fall into two groups, represented by the two lines drawn in the figures. These two lines correspond to the data of April 7, and of April 8, which are typical of the two groups respectively. A key to the cause of these two groups of values is found in the results of April 7 (Fig. 23). The longer curve was obtained in the morning; the vacuum was poor, and the potential was raised by pumping, running up to a maximum. After being once thoroughly exhausted, the tube had an excessively slow rate of leak, so that after lunch hour the potential was still up to 3.25 K.V. and rose steadily, due to the discharge alone and *without pumping*, to 5.45 K.V., when pumping was begun. Throughout the region where the potential rise was automatic the points representing these data fall considerably below those obtained in the morning; approaching them after pumping is begun. The next day the potential had fallen to 0.78 K.V., but the rise of potential was slow and automatic up to 5.45 K.V., where pumping was begun. This curve also falls below the first of those taken the day before, but it *coincides* with the second. Examination of the data reveals that all those of the second (lower) group of values (those of Jan. 21, Apr. 7 (P.M.), and Apr. 8) were taken under conditions of automatic potential rise; and that all those of the first (upper) group were obtained by pumping to raise the potential. The January 21 values start out in good agreement with the lower group, but fall increasingly below them above 3.3 K.V. Since this case is a

"freak"; *i. e.*, it has occurred in the data but the once, it will have to be disregarded until some later work may throw some light upon it.

It seems more probable that the difference in these two sets of curves, which seems to correspond to the difference that Veazey observed as a difference between a freshly obtained vacuum and a long maintained one. is not due to the causes he suggests (an oxidation or other change of the surface of the specimen) but to a difference in the state of the residual gas in the tube; either a difference in the pressure under the different conditions of discharge, or a difference in the character of the gas, due to vapors, or to formerly surface occluded gas, or both. The differences are most marked in the lower range of values, where the difference of absorption and scattering of the electrons due to the differences of the gas state might be sufficient to account for the lowering of the values in the case of the second group.

At the time, no observations were made of the gas pressure conditions, except those indications gotten by observation of the discharge; and these were not reliable, since the form of the tube was so different from the usual one. Since then, a McLeod gauge has been attached and the gas pressure observed under the conditions of taking the first group of values (potential raised by pumping) and the characteristic pressure-potential curves were obtained. Between the potentials 1.00 and 13.00 K.V. the pressure varied between outside limits of 100 and 10μ (thousandths of mm. of mercury). To a crude approximation, the pressure is inversely proportional to the potential through this range. The seal of the new vacuum system was not sufficiently perfect to obtain the conditions of the second set of values. *Indications* of the pressure conditions of this set were obtained, however, in that a measurable *rise* of potential was observed during an appreciable *rise* of pressure. The suspicion is that the "automatic" rise of potential occurred with at the most only a slight decrease of pressure. The greater gas density would cause a greater absorption of energy, etc., and this would explain why the curves obtained in this manner lie below the others.

Only fragmentary data concerning absorption and scattering of kathode rays are available. Extrapolation of values from a table given by Lenard indicates that for the values obtained in group one (upper), L/I at 1 K.V. is about seven times too small, while L/I at 4 K.V. is about 11 per cent. low, and above 4 K.V. the losses are negligible. This does not affect the conclusions drawn from the shape of the curves: As seen in Fig. 22, where the values based on the extrapolation are represented by the dash line, the curvature is just as pronounced, and the existence of an appreciable "minimum" potential is still less evident. Also,

the magnitude of the losses is such that, taken together with the assumption that the "automatic" rise of potential is accompanied by but a slight change of gas pressure, it could quite well account for the difference between the two groups of curves. Later work with this apparatus may be undertaken to obtain more complete data on the absorption and scattering losses. But a much simpler method of obtaining the exact relation between the variables is to use a modern hot kathode discharge tube, since in such a tube the gas density is so small as to cause but an immeasurable amount of loss. This work is now under way.

There will still be present another cause of error to consider; namely, the static potential which accumulates on the specimen and results in causing a reduction of the velocity of the electrons as they approach it. Since the $L - I$ curves at constant V are straight, this static potential would seem to be dependent only upon the gas pressure, if indeed it is a variable. So that in the new apparatus it should be a constant. It seems probable that the appearance of the fluorescent area, reported by Veazey and illustrated in Fig. 14, is due to this static potential. It would be naturally greater at the center, where the chance for leakage is the less, and hence cause a greater decrease in the velocity of the electrons striking there, and also deflect some of the approaching electrons towards the outer annular ring.

The processes of fluorescent radiation are too complex and too little understood to permit the derivation of any theoretical equation against which to check these results. The results themselves suggest vaguely a number of qualitative theoretical explanations, and several empirical (expotential) equations have been tried in an attempt to arrive at some definite conclusions. But the net result of it all is the conclusion that further work is necessary, along lines suggested by the experimental results and by these theoretical speculations, before any definite theory can be developed that will stand rigid scrutiny.

Conclusion.

This investigation of the kathodo-fluorescence of willemite has had as its purpose a determination of the relation between the intensity of fluorescence L, the rate of impact of the kathode electrons (measured by the kathode ray current I), and the electronic kinetic energy (measured by the discharge potential V).

A direct proportionality is found between L and I at constant values of V, confirming the results of previous investigators.

The relation between L/I and V (which corresponds to the relations obtained by Veazey and others between L and V at constant values of I)

is found to be non-linear, of the form shown by the curves plotted; these curves having an increasing slope as the potential is raised, which approaches a constant value for higher potentials, and possibly falls off for values still higher (as indicated by Veazey's results, which are in fair agreement with the present ones). There is no indication of a minimum potential below which no fluorescence would be produced.

The results have been shown to be in general agreement with the *data* obtained by Lenard for similar substances, but to be not in agreement with the empirical relation postulated by him. Indeed, they may be considered as a very definite disproof of that relation.

Certain discrepancies observed by Veazey have been observed in greater detail, under conditions that permit them to be explained as most probably due to the effects of absorption and scattering of the energy of the kathode electrons by the residual gas in the tube.

Static potentials acquired by the specimen are suggested as explaining the uneven appearance of the fluorescence, noticed by Veazey.

Sources of error are recognized in the two paragraphs above: losses due to absorption and scattering, and to static potentials on the specimen. Means for their elimination are being considered.

While the present work has furnished some very promising germs for a theoretical explanation, yet it is but idle speculation to attempt to develop them into any concrete form without first planting them in a very much more fertile soil of experimental investigation. Suffice they now to point the way to that investigation.

THE NECESSARY PHYSICAL ASSUMPTIONS UNDERLYING A PROOF OF THE PLANCK RADIATION LAW.[1]

BY F. RUSSELL V. BICHOWSKY.

IT is usually assumed that in order to prove the Planck radiation law it is necessary to assume some sort of quanta, that is, that it is necessary to assume that some at least of the quantities connected with the distribution of energy in the spectra of a black body have physical significance only for the values E, $2E$, $3E$, etc., all intermediate values, say $\frac{1}{2}E$, being impossible. There is, however, considerable disagreement as to just what the quantities are which thus occur in quanta. Einstein[2] assumes that radiant energy itself is atomic in structure, Planck[3] that matter (oscillators) is such that it can only give out energy in quanta, while Larmor[4] makes the physically somewhat indefinite assumption of equal regions of probability. But in spite of these differences of detail almost everyone assumes that quanta of some sort are necessary for a proof of Planck's law. Indeed, Jeans[5] and also Poincaré[6] have undertaken to prove as much. However, their proof of this point, and indeed all possible proofs connecting the quantum hypothesis with the Planck law are vitiated by the fact that they all make a far more dubious assumption than the one they attempt to justify. For in the course of their proof they assume, as indeed it can be proved they must assume, that the radiating system has the statistical properties of a perfect gas, for once one accepts at the same time both Planck's law and the quantum hypothesis, Maxwell's distribution law (which may be considered the definition of the statistical properties of a perfect gas) follows directly. Putting Planck's equation for the distribution of energy among the different degrees of freedom in any given system in the form

$$\bar{E}_a = \frac{E_0}{e^{-\beta E_0} - 1}, \tag{1}$$

where $\bar{E}_a$ is the average energy per degree of freedom for any frequency

[1] Read at the Washington meeting of the American Physical Society, April 21, 1917.

[2] Ann. d. Physik, IV., 556 (1901).

[3] Dynamical Theory of Gases, Cambridge, 1916, p. 405.

[4] Roy. Soc. Proc., Ser. *A*, *83*, 92 (1909).

[5] Ann. d. Physik, *17*, 132 (1905); *20*, 197 (1906); *22*, 180 (1907).

[6] Journ. de Phys. [5], *2*, 5 (1912). Dernierès Penseès, Paris, Ch. VI., "L'hypothèse des Quanta."

(ν_a) and the constant E_0 replaces the $h\nu$ of the more familiar form (E_0 is of course only constant for a given frequency ν_a) and expanding by long division we get:[1]

$$\bar{E}_a = e^{+\beta E_0} + e^{+2\beta E_0} + \cdots + e^{+n\beta E_0}. \tag{1a}$$

But we have the condition

$$N = (n' + n'' + n''' + \cdots n^{(n)}) \tag{2}$$

(where N is the total number of degrees of freedom and n', n'', etc., are the number of degrees of freedom having respectively the energies $\gamma E'$, $\gamma E''$, etc., γ being an arbitrary constant) and also the condition

$$\bar{E}_a = \bar{E}_a N = \alpha(n'E' + n''E'' + \cdots), \tag{3}$$

where $\bar{E}_a$ as before is the average energy, E_a the total energy. (This equation asserts that the total energy equals the sum of the energies of its parts.) ($E^{(n)}$ does not necessarily have the dimensions of energy though of course $\alpha E^{(n)}$ does.)

Now if we assume the quantum theory it is equivalent to assuming that the values E', E'', etc., equal respectively E_0, $2E_0$, $3E_0$, etc., and hence we have from equation (3) (μ being another arbitrary constant)

$$\bar{E}_a N = \mu(n'E_0 + n''2E_0 + n'''3E_0 + \cdots). \tag{4}$$

But n', n'', n''', etc., are in general some function of E', E'', etc., and since our system will be supposed to be large enough so that the law of distribution does not depend on the size of the system n', n'', etc., will always be the same function (f) of E', E'', etc., hence

$$N\bar{E}_a = \mu\{E_0 f(E_0) + 2E_0 f(2E_0) + \cdots + nE_0 f(nE_0)\} \tag{3}$$

and

$$N = f(E_0) + f(2E_0) + \cdots f(nE_0). \tag{4}$$

But the solution for $f(nE_0)$ consistent with equations (1a), (3) and (4) turns out to be

$$W_a^{(n)} = \frac{n^{(n)}}{N} = f(nE_0) = e^{-\beta nE_0}. \tag{5}$$

But this is merely the familiar form of the Maxwell distribution law where $W_a^{(n)}$ represents the probability of a degree of freedom having the

[1] It is impossible to consistently carry any of the usual quantum theory proof of the radiation law beyond the derivation of equation (1) or (1a). To evaluate E_a or U_a ($U_a = E_a/V$) requires counting up the total number of degrees of freedom in a black body, and this can only be done by using Fourier's analysis, but Fourier's analysis is explicitly based on the assumption of continuous energy radiation, and cannot be applied to radiation in quanta.

value nE_0, which shows that instead of the quantum theory being a necessary consequence of the Planck law one cannot prove Planck's law from the single assumption of the quantum hypothesis but must necessarily make the further and arbitrary assumption that Maxwell's law holds for the local distribution of values of those coördinates fixing the distribution of radiant energy in a black body at steady state. If you fail to make the Maxwell assumption the radiation law can not by any mathematical process be derived from the quantum theory. Or putting our result in other terms, the three propositions: (*a*) Planck's law represents the facts, (*b*) the quantum theory is true, (*c*) Maxwell's law holds for the system in question; are not independent. If you assume any two the other follows. The establishment however of the truth (or falsity) of only one of these statements implies nothing whatsoever about either the truth or falsity of the others.

Now most of the criticism that has been rained on the Planck equation has had to do not with the Maxwell's law assumption but with the quantum hypothesis. But this, at least in my opinion, has simply confused the issue. The really doubtful part of the present derivation of the Planck law is the assumption that Maxwell's law holds. That is, the assumption that the distribution of the values of the coördinates is a function only of the single variable $n\beta E_0$ (which we may speak of as the generalized energy per wave-length). If this assumption were true it is easy to show that the radiation in a black body should obey the perfect gas laws. This being the case, since we know both theoretically and from actual experiment that equipartition must hold for a perfect gas, and since we have (if Maxwell's law holds) in a radiating system a condition exactly analogous to the distribution of momenta in a perfect gas; it is quite inconceivable that equipartition and hence the Rayleigh-Jeans distribution law, should not hold for radiation. It is the assumption of the truth of Maxwell's law as applied to the case of a radiating system, and not the assumption of quanta that contradicts classical mechanics and this in a far more grievous manner than has usually been assumed, for after all the basis of the Hamiltonian equations and hence of the equipartition law for a perfect gas is nothing more or less than the assumption that the dynamical system can be reduced to parts whose motions obey the law of the simple pendulum, *i. e.*,

$$\frac{dp_s}{dt} = -\frac{\delta E}{\delta q_s}$$

and if this assumption is not true for the system " Radiation in equilibrium with a black body " by what juggling is the vibratory theory

of light to be justified? If one wishes further confirmation of the fact that the fairly innocuous though quite needless assumption of quanta does not by itself contradict classical mechanics he should observe an automatic weighing machine. It is obvious that, given the proper kind of a system to produce them, quanta of energy or anything else could exist. My objection to the Planck law is that the kind of system assumed is not a proper kind of system.

Obviously a system which is going to act as a weighing machine must have certain properties. If you are going to transfer a continuous variable into a discontinuous variable, you must have some sort of a reserve stock. If energy comes in a continuous stream and goes out in quanta there must be between periods of discharge a heaping up of energy. Thus it is necessary to assume some sort of reserved or bound energy different from the free energy of radiation.

But this Maxwell's law does not allow. The physical bases for Maxwell's law or any law of that form are the two definitions:

(1) The system is in a steady state.

(2) The property distributed according to Maxwell's law is conservative

(with which we will not be greatly interested) and the physical assumption:

(3) No restrictions hold other than (1) and (2).

In mathematical form this condition is:

$$\delta Q_a = \delta\left(\frac{N_a}{N_a' N_a'' N_a''' \dots}\right) = 0.$$

It is this condition to which your attention is invited, for it forms the Achilles' heel of the quantum argument. If no other conditions hold in a radiating system than (1) and (2) the distribution of energy is a function only of the energy density of the system. This besides requiring equipartition makes it impossible to explain the mechanism of quantum emission as that mechanism requires a distinction between the bound energy of the system and the total energy (without which, by the way, transfer of energy from wave-length to wave-length could not take place). In other words it requires that W_a be a function not only of E but of some other variable, say Ψ. Unfortunately, due to our lack of experimental data in regard to mechanism of radiation transfer, it is not possible to give an absolute solution for this function. Gibbs, however, with almost preternatural foresight has given us the simplest form that such a function may take in his formula for canonical distribution, namely,

$$W_a = e^{\frac{+\Psi-\epsilon}{\theta}}.$$

This form corresponds to the assumption, say that coördinates determining energy values between O and E determine the total energy of the system and coördinates fixing energy values between O and some values less than E, say E_0, fix the bound energy of the system (the energy associated with ankylosed coördinates). In other words Gibbs's assumption is for the radiation case equivalent to assuming that radiation (free energy) of a system cannot be generated until the magnitude of the coördinates reach a certain value, say E_0. From here on, however, radiation will be continuous. And thus in the proper sense of the word no quantum theory is needed. If we make Gibbs's assumption it is easy to show, as indeed Ratnowsky[1] has already shown, that the Planck radiation law follows directly and this without the assumption of quanta (you assume instead a threshold value), without the assumption of discontinuities, without necessitating the giving up of infinitesimal analysis (as of course the quantum theory requires), without contradicting classical mechanics, without contradicting the very cogent experimental evidence of Duane and others that shows very plainly that quanta have no physical existence, and with the very great advantage that the one physical assumption made, namely, that radiation is given off only when the energy of the system has become greater than a given threshold value E_0 and from there on is given off continuously, is of itself very probable.[2]

APPENDIX.

The Entropy Equation of Solid Bodies and Gases and the Universal Quantum of Activity.[3]

By Simon Ratnowsky.

Let $q_1, q_2, \cdots, q_n$ equal the generalized coördinates which determine the state and configuration of the system, and let $q_1, q_2, \cdots, q_n'$ be the generalized velocities, then

$$p_1 = \frac{\partial \epsilon}{\partial \dot{q}_1}, \cdots, \cdots, p_n = \frac{\partial \epsilon}{\partial \dot{q}_n}$$

represent the generalized momenta where ϵ is the total energy of the system, the value. $q_1, \cdots, q_n, p_1, \cdots, p_n$ fix a particular state (phase) of the system. It is, therefore, possible to plot the state of such a system by means of a single point in a $2n$-dimensional space.

[1] Ber. d. D. Phy. Ges., *16*, 232 (1916); see appendix for a translation.

[2] Appended to this article is a translation of a part of Ratnowsky's original proof. It is possible to make a more direct and perhaps more rigorous derivation of the Planck equation on this basis than Ratnowsky has given, but since Ratnowsky's article has, because of the war, become practically inaccessible to American readers it has been thought worth while to republish the proof in its original form.

[3] Ber. d. D. Phy. Ges., *16*, 232 (1916). Translated by F. Russell v. Bichowsky. Only the mathematical part of Ratnowsky's paper is given here. The last part of the proof has been greatly abbreviated.

Following Gibbs a totality (N) of systems is canonically distributed when the number of systems in an element of the phase space $d\lambda = dq_1, \cdots, dq_n, dp_1, \cdots, dp_n$ is given by the equation

$$s(p, q)d\lambda = N e^{\frac{\Psi-\epsilon}{\Theta}} d\lambda (s = \text{distribution density}), \tag{1}$$

where Θ and Ψ are two constants which have a definite thermodynamic meaning. The constant, Θ, which after Gibbs will be called the modulus of the distribution, is proportional to the absolute temperature, ($\Theta = kT$, where $k = 1.347 \times 10^{-16}$), and Ψ is the statistical free energy which is identical with the thermodynamic free energy of any actual system.

Since $sd\lambda$ is the number of systems in an element, $d\lambda$, of phase space it follows that $sd\lambda$ integrated over the whole phase space must give the total number of systems (N), that is

$$\int sd\lambda = N \int, \cdots, \int e^{\frac{\Psi-\epsilon}{\Theta}} dq_1, \cdots, dq_n, dp_1, \cdots, dp_n = N \tag{2}$$

and Ψ, therefore is defined by the equation,

$$\int, \cdots, \int e^{\frac{\Psi-\epsilon}{\Theta}} dq_1, \cdots, dp_n = 1$$

or,

$$e^{-\frac{\Psi}{\Theta}} = \int, \cdots, \int e^{-\frac{\epsilon}{\Theta}} dq_1, \cdots, dp_n.$$

From this equation Ψ may be calculated whenever ϵ is given specifically as a function of $q_1, \cdots, p_n$. If, for instance, ϵ is given by the equation

$$\epsilon = \frac{f}{2}(q_1^2 + q_2^2 + \cdots + q_n^2) + \frac{1}{2m}(p_1^2 + \cdots + p_n^2).$$

we can write:

$$e^{-\frac{\Psi}{\Theta}} = \int, \cdots, \int e^{-\frac{1}{\Theta}\left\{\frac{f}{2}(q_1^2+\ldots+q_n^2)+\frac{1}{2m}(p_1^2+\ldots+p_n^2)\right\}} dq_1, \cdots, dp_n.$$

If the integration limits of the variables

$$(q_1, p_1), (q_2, p_2), \cdots, (q_n, p_n)$$

are independent by pairs this multiple integral can be factored into

$$e^{-\frac{\Psi}{\Theta}} = \int\int e^{-\frac{1}{\Theta}\left(\frac{f}{2}q_1^2+\frac{1}{2m}p_1^2\right)} dq_1 dp_1 \cdots \int\int e^{-\frac{1}{\Theta}\left(\frac{f}{2}q_n^2+\frac{1}{2m}p_n^2\right)} dq_n dp_n \tag{3}$$

and

$$\Psi = -\Theta \log \int\int e^{-\frac{1}{\Theta}\left(\frac{f}{2}q_1^2+\frac{1}{2m}p_1^2\right)} dq_1 dp_1 \cdots \int\int e^{-\left(\frac{g}{2}q_n^2+\frac{1}{2m}p_n^2\right)} dq_n dp_n.$$

If the integration is carried out over all possible values of the variables between $-\infty$ and $+\infty$ the total free energy of the system can be calculated and this totally independent of what the nature of this energy is and of from what energy reservoirs it is drawn.

Now, without further inquiring about the inner mechanism of the system we will make the purely formal assumption that the energy of the system is of a two-fold nature: the one kind the energy which is the so-called heat energy (except that borrowed from the energy reservoirs), the other kind of energy, the proper energy of the system. Since the total energy (heat energy plus proper energy) can have all possible values and since in order to calculate Ψ by means of equation (3), the integration must be taken over all possible phases, therefore, if we are to calculate that part of $\Psi(\Psi_0)$ which corresponds to the proper energy, the phase space must be limited by some special assumption. This limitation must of course agree with the hypothesis of proper energy and must indeed follow as its consequence, we will,

therefore, further define our assumption of proper energy. That is, we will make a special hypothesis in regard to the proper energy, namely, that the amount of proper energy of any degree of freedom cannot be more than a certain fixed amount, say ϵ_0, or in other words we will assume that for every degree of freedom there is a limiting value for the proper energy.

If we take for the variables of equation (3) instead of $q_1, p_1, \cdots, q_n, p_n$, the energy of a single degree of freedom

$$\epsilon_i = \frac{f}{2}(q_i)^2 + \frac{1}{2m}(p_i)^2$$

we will get the total free energy of the system if we integrate between o and $+\infty$. On the other hand, we will get that part of the "free energy" of the system which belongs to the proper energy of the system if we carry out the integration only over the possible variations of the proper energy, that is, if we carry out the integration not over the entire phase space (which is unlimited) but only over that part of the phase space which we have limited by our restriction. In the light of this restriction we can define Ψ_0 as follows:

$$e^{-\frac{\Psi_0}{\Theta}} = \int\int e^{-\frac{1}{\Theta}\left(\frac{f}{2}q_1^2+\frac{1}{2m}p_1^2\right)}dq_1dp_1\cdots\int\int e^{-\frac{1}{\Theta}\left(\frac{f}{2}q_n^2+\frac{1}{2m}p_n^2\right)}dq_ndp_n$$

$$\left(\frac{f}{2}q_i^2+\frac{1}{2m}p_i^2 \leqq \epsilon_0\right)$$

$$= \left\{\int\int e^{-\frac{1}{\Theta}\left(\frac{f}{2}q^2+\frac{1}{2m}p^2\right)}dqdp\right\}^n \qquad (4)$$

$$\left(\frac{f}{2}q_i^2+\frac{1}{2m}p_i^2 \leqq \epsilon_0\right)$$

where we make the simplification that the limiting value of the proper energy is the same (ϵ_0) for each degree of freedom.

For the heat energy, (Ψ_1), then $\Psi - \Psi_0 = \Psi_1$. Ψ_1 is also defined from (3) and (4)

$$e^{-\frac{\Psi}{\Theta}} = e^{-\frac{(\Psi-\Psi_0)}{\Theta}}$$

$$= \frac{\int\cdots\int e^{-\frac{\epsilon}{\Theta}}dq_1\cdots dp_n}{\left\{\int\int e^{-\frac{1}{\Theta}\left(\frac{f}{2}q^2+\frac{1}{2m}p^2\right)}dqdp\right\}^n} = \frac{\left\{\int\int_{-\infty}^{+\infty} e^{-\frac{1}{\Theta}\left(\frac{f}{2}q^2+\frac{1}{2m}p^2\right)}dqdp\right\}^{2N}}{\left\{\int\int e^{-\frac{1}{\Theta}\left(\frac{f}{2}q^2+\frac{1}{2m}p^2\right)}dqdp\right\}^{3N}}$$

$$\left(\frac{f}{2}q^2+\frac{1}{2m}p^2 \leqq \epsilon_0\right) \qquad \left(\frac{f}{2}q^2+\frac{1}{2m}p^2 \leqq \epsilon_0\right),$$

where we have placed $n = 3N$. Now, if we take as the variable, ϵ, we can write

$$\int\int e^{-\frac{1}{\Theta}\left(\frac{f}{2}q^2+\frac{1}{m^2}p^2\right)}dqdp = 2\pi\Theta\sqrt{\frac{m}{f}}\int e^{-x}dx,$$

where $\epsilon/\Theta = x$, and also

$$e^{-\frac{\Psi_1}{\Theta}} = \frac{\left\{2\pi\Theta\sqrt{\frac{m}{f}}\int_0^{\infty} e^{-x}dx\right\}^{3N}}{\left\{2\pi\Theta\sqrt{\frac{m}{f}}\int_0^{x^0} e^{-x}dx\right\}^{3N}}. \qquad (4a)$$

If we carry out this simple integration, we have

$$e^{-\frac{\Psi_1}{\Theta}} = \frac{1}{\left(1-e^{-\frac{\epsilon_0}{\Theta}}\right)^{3N}},$$

where

$$\frac{\epsilon_0}{\Theta} = x_0$$

and hence

$$\Psi_1 = 3N\Theta \log \left(1 - e^{-\frac{\epsilon_0}{\Theta}}\right)$$

or since $\Theta = kT$

$$\Psi_1 = 3N\,kT \log \left(1 - e^{-\frac{\epsilon_0}{kT}}\right).$$

The quantity Ψ_1 has the meaning of free energy, therefore, we can make the usual calculation of total energy, pressure and entropy from the well-known equations of thermodynamics, namely:

$$S = \frac{\delta F}{\delta T} = \frac{\delta \Psi}{\delta T}; \qquad U = F - T\frac{\delta F}{\delta T}; \qquad P = -T\frac{\delta F}{\delta V};$$

from these equations we obtain for the entropy

$$S = 3Nk \frac{\frac{\epsilon_0}{kT}}{e^{\frac{\epsilon_0}{kT}} - 1} - \log \left(1 - e^{-\frac{\epsilon_0}{kT}}\right) \tag{5}$$

and for the energy U

$$U = 3N \frac{\epsilon_0}{\left(e^{\frac{\epsilon_0}{kT}} - 1\right)}. \tag{6}$$

From (4) and (4a)

$$e^{-\frac{\Psi_0}{\Theta}} = \left\{\Theta 2\pi \sqrt{\frac{m}{f}} \int_0^{x_0} e^{-x} dx\right\}^{3N}$$

where $x_0 = \epsilon_0/kT$; $\Theta = kT$ and $2\pi\sqrt{(m/f)} = 1/\nu$. Therefore,

$$e^{-\frac{\Psi_0}{kT}} = \left\{\frac{kT}{\nu} \int_0^{x_0} e^{-x} dx\right\}^{3N}$$

and

$$\Psi_0 = -3NkT \log \frac{kT}{\nu} (1 - e^{-\frac{\epsilon_0}{kT}});$$

from this since $S_0 = -(\delta\Psi_0/\delta T)$ we get

$$S_0 = 3Nk \left\{ \frac{\frac{\epsilon_0}{kT}}{e^{\frac{\epsilon_0}{kT}} - 1} - \log (1 - e^{-\frac{\epsilon_0}{kT}} - 3Nk \log \frac{\nu}{kT} + 3Nk. \right. \tag{7}$$

Now if ϵ_0/kT is very small, that is, if $kT \gg \epsilon_0$

$$S_0 = 3Nk \left\{1 - \log \frac{\epsilon_0}{kT}\right\} = 3R \log T + 3R - 3R \log \frac{\epsilon_0}{k}$$

where

$$R = kN.$$

Now according to the classical thermodynamics

$$S = 3R \log T + S'.$$

But from (7) if $kT \gg \epsilon_0$

$$S_0 = 3kN \log \frac{\epsilon_0}{\nu}.$$

Therefore ϵ_0/ν = a universal constant $= h$ and

$$\epsilon_0 = h\nu. \tag{8}$$

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ON CERTAIN ABSORPTION BANDS IN THE SPECTRA OF THE URANYL SALTS.

BY H. L. HOWES.

PROBABLY Mr. G. C. Stokes[1] was the first investigator to notice that the fluorescence and absorption spectra of the uranyl salts are slightly overlapped.

Morton and Bolton[2] also noticed coincidences in the position of several fluorescence and absorption bands of the uranyl salts.

J. Becquerel and Onnes[3] working at low temperature found several coincidences in the positions of the narrowed bands.

Nichols and Merritt[4] found that the "reversing region" was of considerable length; in the case of uranyl potassium sulphate they were able to reverse the brilliant fluorescence band at 5,130 Å. u. whereas previously the reversals had been limited to the region beyond 5,000 Å. u.

In our study of the uranyl double chlorides Prof. E. L. Nichols and the writer found it possible to reverse a complete group of fluorescence bands lying between 5,080 Å. u. and 4,880 Å. u. The desire to extend this "reversing region" towards the red led the writer to undertake the present investigation. A theory of luminescent radiation very recently proposed by Dr. E. H. Kennard also made the investigation of interest.

Since the crystals are of a greenish yellow color they become rapidly transparent as the light admitted is changed from blue to yellow. This necessitates the use of crystals of increasingly thicker layers to bring out the dimmer absorption bands. To a certain extent the crystal acts as a screen to absorb the blue light which would cause fluorescence, nevertheless it was found necessary to interpose orange or yellow screens of different densities to eliminate fluorescence in a region where ordinarily it is at a maximum. At first the colored glasses made by the Corning Glass Company were used as filters; later, solutions of potassium bichromate of varying concentration. It is evident that the screening must be constantly changed when light from the arc is used as a back-

[1] G. C. Stokes, Phil. Trans., 1852, p. 463.

[2] Morton and Bolton, Chem. News, pp. 47, 113, etc. (1873).

[3] J. Becquerel and Onnes, Leiden Communications, No. 110, 1909.

[4] Nichols and Merritt, PHYS. REV., Vol. 33, Nov., 1911, p. 354.

ground for bands of increasingly longer wave-length. It was thought that a beam of monochromatic light could be used as a background and thus obviate exciting the crystal to fluorescence, but a preliminary study by Dr. D. T. Wilber and the writer indicated that such a beam of dispersed light could not be made of sufficient intensity to bring out the dimmer bands.

In Fig. 1 is pictured a portion of the fluorescence and absorption

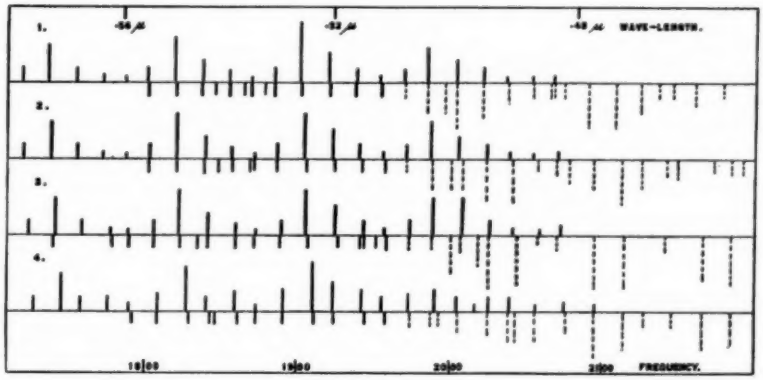

Fig. 1.

Fluorescence bands are indicated by lines above the horizontal. Old absorption bands are indicated by dotted bands below the line; new absorption bands by *solid* bands below the horizontal.

The plot shows only a portion of the complete spectra of the following salts at + 20° C.

1. Potassium uranyl chloride.
2. Ammonium uranyl chloride.
3. Rubidium uranyl chloride.
4. Caesium uranyl chloride.

spectrum of each of the double chlorides studied. Fluorescence bands are designated by heavy lines above the horizontal line. The older, well-established absorption bands are designated by dotted lines below the horizontal and the new bands by solid lines below the horizontal. The relative positions of the fluorescence and absorption bands are readily seen. An examination of Table I. will indicate more definitely, in frequency numbers, the agreement or lack of agreement in position. In the third and fourth columns are given the well-established fluorescence and absorption band series. At + 20° almost all of the new bands fall into fluorescence series while at − 185° the new bands generally fall in the absorption band series. Table II. gives the new bands at − 185°.

The rôle played by these new bands in producing fluorescence is a minor one, because they are excessively dim. No doubt if special

crystals of great size and exceptional clearness were formed the bands would appear stronger, and more bands could be discovered. The present study has added the reversals of two complete groups to the original group mentioned. For some reason the bands can not be traced as far into the red when the crystal is cooled to $-185°$. It is evident that Stokes's law does not hold and it may be that every fluorescence band has an absorption band of the same wave-length.

TABLE I.

New Absorption Bands at + 20° C.

Potassium Uranyl Chloride.				Ammonium Uranyl Chloride.			
Absorption.	Fluorescence.	Fluorescence Series.	Absorption Series.	Absorption.	Fluorescence.	Fluorescence Series.	Absorption Series.
1802.1	1801.4	*B*	.....	1802.5	1803.1	*B*	.....
1820.2	1819.3	*C*	.....	1820.8	1820.7	*C*	.....
1836.5	1837.6	*D*	.....	1838.9	1839.7	*D*	.....
1846.0	.....	.....	*c*	1848.8	.....	.....	*c*
1855.3	1855.3	*E*	.....	1857.8	1856.9	*E*	.....
1865.0	.....	.....	*d*	1869.2	.....	.....	*d''*
1869.4	1869.6	*A*	.....	1871.8	1871.8	*A*	.....
1879.0	.....	.....	*e*	1886.5	1886.8	*B*	.....
1885.1	1884.7	*B*	.....	1906.2	1904.6	*C*	.....
1902.2	1901.5	*C*	.....	1924.2	1923.2	*D*	.....
1920.9	1920.1	*D*	.....	1942.3	1940.5	*E*	.....
1937.6	1938.3	*E*	.....	1957.4	1956.3	*A*	.....
1954.7	1953.5	*A*	.....				

Rubidium Uranyl Chloride.				Cæsium Uranyl Chloride.			
Absorption.	Fluorescence.	Fluorescence Series.	Absorption Series.	Absorption.	Fluorescence.	Fluorescence Series.	Absorption Series.
1740.0	1741.6	*C*	.....	1791.5	1789.7	*A*	.....
1778.7	1777.8	*E*	.....	1808.0	1808.6	*B*	.....
1789.5	1789.4	*A*	.....	1829.2	1827.5	*C*	.....
1806.1	1806.1	*B*	.....	1843.0	1840.5	*D*	.....
1823.2	1822.8	*C*	.....	1846.4	.....	.....	*β*
1834.9	.....	.....	*b*	1861.2	1859.1	*E*	.....
1841.6	1841.5	*D*	.....	1873.0	1873.1	*A*	.....
1859.8	1859.8	*E*	.....	1890.7	1891.1	*B*	.....
1872.0	1873.1	*A*	.....	1911.1	1910.4	*C*	.....
1889.0	1890.0	*B*	.....	1923.8	1923.6	*D*	.....
1907.2	1905.5	*C*	.....	1944.4	1942.7	*E*	.....
1926.7	1925.0	*D*	.....	1957.8	1955.7	*A*	.....
1941.7?	.....	.....	*d*				
1944.0	1943.5	*E*	.....				
1952.0?	.....	.....	*e*?				
1958.7	1957.1	*A*	.....				

Table II.

New Absorption Bands at − 185° C.

Potassium Uranyl Chloride.				Ammonium Uranyl Chloride.			
Absorption.	Fluorescence.	Fluorescence Series.	Absorption Series.	Absorption.	Fluorescence.	Fluorescence Series.	Absorption Series.
1941.7	1940.0	E_2'	d_2	1945.9	1945.0	E_2''	d_2''
1947.6	.....	.....	e_1	1953.5	1953.7	A_1	e_1
1954.7	.....	.....	e_2'	1956.6	.....	.....	.....
1960.4	.....	.....	b_1'	1963.5	.....	.....	e_2''
1965.8	1963.9	B_1	a_1	1967.7	1968.7	B_1	b_1
1972.4	1972.3	B_2	b_2	1973.6	.....	.....	b_2'
1977.5	1977.8	B_3	b_3	1977.1	1977.9	B_2	b_2
1984.9	.....	.....	c_2'	1981.0	.....	.....	b_2''
1989.3	.....	.....	c_2''	1984.9	.....	.....	b_3
1998.0	1997.2	D_1	d_1	1992.0	1992.7	C_2	c_2
2008.8	2007.4	D_2	d_2	1996.8	.....	.....	.....
				2002.8	.....	.....	d_1'
				2006.8	.....	.....	d_1''
				2014.1	.....	.....	d_2''

Rubidium Uranyl Chloride.				Cæsium Uranyl Chloride.			
Absorption.	Fluorescence.	Fluorescence Series.	Absorption Series.	Absorption.	Fluorescence.	Fluorescence Series.	Absorption Series.
1944.4	.....	.....	d_2''	1953.9	.....	.....	d_2''
1952.4	.....	.....	e_1'	1956.6	.....	.....	.....
1954.7	.....	.....	.....	1958.9	.....	.....	e_2'
1958.1	1957.9	A_1	e_2'	1967.0	.....	.....	a_1'
1963.9	.....	.....	a_1'	1970.8	.....	.....	.....
1973.9	.....	.....	b_1''	1974.3	.....	.....	b_1'
1981.0	.....	.....	b_2	1978.2	.....	.....	b_1''
1985.7	.....	.....	.....	1982.9	.....	.....	b_2'
1995.6	.....	.....	c_2	1987.7	.....	.....	b_2''
2005.2	2003.7	D_1	d_1	1991.3	.....	.....	b_3
2010.1	.....	.....	d_2'	1997.6	1997.6	C_1	c_1
2016.1	.....	.....	d_2''	2005.6	.....	.....	c_2
				2009.6	2008.5	D_1	d_1
				2016.1	2014.9	D_2'	d_2'
				2022.2	.....	.....	d_2''

Physical Laboratory of Cornell University,
August 31, 1917.

RESONANCE RADIATION OF SODIUM VAPOR EXCITED BY ONE OF THE D LINES.

BY R. W. WOOD AND FRED L. MOHLER.

INTRODUCTION.

THE purpose of this investigation was to study the resonance spectrum of sodium vapor when the resonance was excited by a single D line. In a paper on "Resonance Radiation of Sodium Vapor"[1] published by one of us in 1905, it was shown that if a bulb containing pure sodium vapor was illuminated by light from a sodium flame, the vapor emitted a yellow light which spectroscopic analysis showed to be identical with the exciting light, in other words, the two D lines. It was suggested at this time that it would be interesting to see if both D lines appeared when the vapor was illuminated by a single D line. This would determine whether the mechanisms that give rise to the D lines are separate or in some way connected.

In 1914 this experiment was tried by Wood and Dunoyer.[2] This experiment was made possible by the discovery of a polarization method of separating close spectral doublets that eliminated the great loss of light involved in a high-power monochromator, but even with this method the resonance light is very faint. The spectrum of resonance excited by D_2 was photographed with exposures varying from 10 to 15 hours. The majority of the plates showed only the D_2 line, but owing to under exposure D_1 would not have been visible if it was less than one fourth of the intensity of D_2. Some plates indeed showed both D_1 and D_2, but the presence of D_1 in the exciting light was judged to be the cause of this. Imperfections in the optical system made it impossible to entirely remove D_1 from the exciting light and as it was sensitive to temperature changes the nature of the transmitted light sometimes changed during an exposure. It was concluded that sodium resonance excited by D_2 consisted of D_2 alone, but the results admit of two other possibilities. D_1 light may always be present though much fainter than D_2, or it may only appear under certain conditions.

Other resonance phenomena show that the radiation centers in sodium are not entirely independent. One of us[3] showed in 1905 that excitation

[1] R. W. Wood, Phil. Mag. (6), 10, 513, 1905.

[2] Wood and Dunoyer, Phil. Mag. (6), 27, 1018, 1914.

[3] Wood, Phil. Mag. (6), 10, 408, 1905.

of sodium vapor by blue-green light, in the region of the band spectrum, gives rise to the D lines, or, at least, to a band in that region.

Strutt[1] in 1915 found that resonance radiation consisting of the D lines could be excited by the 3300 doublet of sodium, the second doublet in the principal series of which the D lines are the first. When only one line of the 3300 doublet was excited by a coincident zinc line both the D lines again appeared. This remarkable discovery, indicating clearly some connection between the emission centers of the doublets of the principal series of sodium, made a further study of the excitation of resonance by one of the D lines seem desirable. In view of results which will be mentioned further along, it may be well to point out that Strutt's results may have been due to the presence of hydrogen in his bulb of sodium vapor.

The arrangement of the apparatus and the method used in the present work differ only in minor details from the method of Wood and Dunoyer.

The chief requirements for the investigation are:

1. A method of completely separating D_1 and D_2 in the exciting light with the least possible reduction in the intensity of the light.
2. The preparation of bulbs containing sodium vapor that will give brilliant resonance during a prolonged heating.
3. The analysis of the light by a spectroscope giving the greatest possible intensity of light commensurate with the dispersion necessary to clearly resolve the D lines.

The Method of Separating the D Lines.

The polarization method of separating close spectrum lines was described by one of us[2] in 1914. Briefly the method is as follows: If plane-polarized monochromatic light is passed through a doubly refracting crystal with its direction of vibration making an angle of 45° with the optic axis of the crystal, it will in general emerge elliptically polarized, but for certain thicknesses of the crystal it will be plane polarized either in the same direction as the incident light or at 90° to this direction. If, now, we have light of two wave-lengths in the incident beam, the emerging beam will be in two different states of polarization due to the difference in refractive index for the two wave-lengths. It is possible to find a thickness of the crystal such that the emergent light consists of two monochromatic beams plane polarized at right angles to each other. By the use of an analyzing nicol either wave-length may be cut out and monochromatic light secured.

[1] R. J. Strutt, Proc. of Royal Soc., Series *A*, 91, p. 511.

[2] Wood, Phil. Mag. (6), 27, 524, 1914.

To cut out one of the D lines with quartz a plate about 32 mm. thick is required. The thickness can vary considerably for the precise optical length of path required can be secured by tilting the plate. To secure intense illumination a large plate of quartz must be used in parallel light and the faces must be optically plane, or nearly so.

Since half of the light is cut out if it is polarized by a nicol, large double-image prisms were used to polarize and analyze the light. They were placed so that only two images of the source were formed. When the quartz block was placed between them and properly oriented three images appeared, the central image consisting of two superposed images containing only D_2 light and two lateral ones containing only D_1 light. A slight tilting of the quartz plate changed the central image to D_1 and the lateral ones to D_2.

The large quartz block measuring $85 \times 60 \times 32$ mms., prepared for the experiment of Wood and Dunoyer, was refigured and supported rigidly in a brass frame arranged to rotate on an axis parallel to the optic axis of the crystal, and inclined at an angle of 45° to the vertical. It was placed between two large Iceland-spar prisms of about the same size as the block of quartz and mounted with their edges (optic axes) vertical. The lenses of a large Dunoyer condenser made the light passing through the prisms parallel, and brought it to a focus on the bulb of sodium vapor.

This optical system was enclosed in a wooden box, which was kept at a constant temperature to within 0.1° C. by a benzene thermostat. This precaution is necessary for a change in temperature of a degree or two will completely change the nature of the light transmitted by the quartz block. A long handle fastened to the supporting rod of the quartz block made it possible for an observer at the spectroscope to turn the block and adjust the apparatus for the extinction of one of the D lines.

THE SPECTROSCOPE.

For analysis of the resonance radiation a large two-prism spectroscope furnished with portrait objectives of 3 inch aperture and 24 inch focus, loaned by the psychology department of this university, was found to give the best results. With this instrument brilliant illumination and clear resolution of the D lines were secured with a fairly wide slit, though the definition was not perfect. This spectroscope had been arranged for use as a monochromator, with the second slit mounted on a screw, so that it could be moved along the spectrum. For the present work the photographic plates were simply clamped against the second slit mounting. This offered a very convenient method of taking a series of exposures on the same plate, side by side instead of one above the other, as in the ordinary plateholder.

Light Source.

The source of light was a Meker burner surrounded by a chimney provided with a rectangular aperture measuring about 2×5 cms. The image of this rectangle, formed by the polarizing separator, was thrown on the bulb of sodium vapor. A disk of asbestos soaked in salt solution touched the edge of the flame and this disk was revolved once in twelve hours by the hour hand gear of a clock. This device kept the sodium flame at about the proper intensity to give the maximum brilliancy of resonance. It is very important, however, to have the disk graze the flame on the side furthest removed from the lens, as by this arrangement reversal of the D lines is obviated. This is of fundamental importance since the resonance radiation is excited by the core of the line only.

Heating Device.

The bulb containing the sodium was supported above an asbestos chimney about two feet high and five inches in diameter, below which was placed a nest of Bunsen burners. The bulb was supported by a wire frame in such a way that it could be turned about a vertical axis, and a firmly supported pin point touched the front surface to detect any possible displacement when the bulb was rotated.

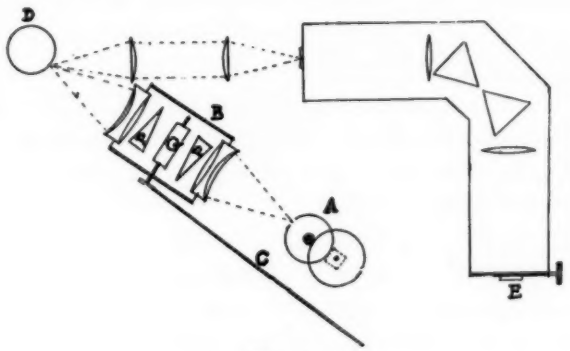

Fig. 1.

Arrangement of Apparatus.

Fig. 1 shows a plan of the apparatus. The light source asbestos disk and surrounding chimney is at *A*. *B* is the optical system for separating the D lines with the long handle *C* to turn the quartz block *Q* between the spar prisms *PP*. The bulb of sodium vapor is at *D*, placed in the position shown so as to prevent directly reflected light from falling on the slit of the spectroscope. At *E* is the plateholder of the spectroscope mounted on a horizontal screw.

The improvements over the apparatus previously used are in the device for separating the D lines and in the spectroscope. The spectroscope gave better illumination and the system for separating the D lines gave almost perfect extinction of D_1, though the extinction of D_2 was not quite so good, as D_2 has double the intensity of D_1 in the case of the comparatively feeble flame used for the excitation.

PREPARATION OF THE BULBS.

The method used in preparing the sodium bulbs is practically that previously described by Dunoyer and Wood.[1] A bulb about 5 cm. in diameter is made as shown in Fig. 2. A piece of sodium, weighing about .2 of a gram, is put in the tube at the left, the tube immediately sealed at *A* and the bulb connected to the pump and exhausted. The bulb is heated for about half an hour to free the glass from occluded water and the sodium is then distilled into it and the side tube sealed off. The sodium is then distilled from one side of the bulb to the other many times by heating opposite sides alternately with a Bunsen burner, while the pump is kept running and the pressure read from time to time on a McLeod gauge.

Fig. 2.

The preliminary heating prevents or at least retards the reaction of the sodium with the glass which at temperatures above 200° reduces the silicon oxide and makes the glass brown and finally opaque. Bulbs of Pyrex glass, which proved to be far superior to ordinary glass in this respect, prepared in the way described, showed scarcely any color after twelve hours' heating at 220°, and were quite transparent, though brown, after heating twelve hours at 300°.

The repeated distillation of the sodium was to drive off the hydrogen which is occluded by it in large quantities. If, after distilling the sodium into the bulb the pump was cut off and the sodium driven from one side of the bulb to the other two or three times the pressure gauge indicated a rise of about .3 mm., and repeated distillation with the pump maintaining a vacuum of about .002 mm., only removed this hydrogen very slowly. The sodium vapor seemed to carry most of the hydrogen with it as it was distilled from side to side of the bulb, for when the pump was stopped and the bulb heated the pressure always increased several hundredths of a millimeter. In the preparation of one bulb the sodium was distilled back and forth across the bulb 170 times in a high vacuum after which the pump was stopped and .01 mm. of gas was

[1] Dunoyer and Wood, Phil. Mag. (6), 27, 1027, 1914.

given off by the sodium when it was heated. In cases in which it was desirable to have some hydrogen present the pump was cut off as soon as the sodium distilled into the bulb. The bulb was then heated, the pressure measured, and the bulb sealed off. To test whether prolonged heating increased the amount of gas some bulbs were opened under mercury after they had been used, but the amount of gas present was not noticeably different.

The careful removal of all the hydrogen is not necessary to secure brilliant resonance, but it does affect the character of the resonance spectrum, as will be explained later.

Procedure.

To facilitate the adjustment of the apparatus for extinction of one of the D lines a patch of magnesium oxide was put on the surface of the bulb by burning magnesium wire below it and then removing all the oxide except a small rectangular strip. To adjust the apparatus the bulb is placed in position and turned until the light from the sodium flame falls on the patch of oxide. As magnesium oxide is a nearly perfect reflector this gives a source of light bright enough to make all adjustments. To photograph the resonance spectrum the bulb is turned slightly till the exciting light falls on clean glass. Care must be taken that no light is directly reflected into the spectroscope.

Owing to the path difference through the quartz block of rays coming from different parts of the rectangular aperture, the illumination is not strictly monochromatic (D_2) over the entire image of the aperture. Experiments showed that we have pure D_2 radiation along slightly curved and nearly vertical strips two or three millimeters in width, the distribution of the illumination being somewhat as shown in Fig. 3.

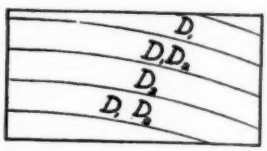

Fig. 3.

The upper and lower portions of the image of the patch of resonance radiation thrown on the slit were excited by both lines when the central portion was excited by one only. For this reason any motion of the image on the slit either during the exposure, or in turning the bulb before the exposure, had to be guarded against. As in some cases only a small part of the line was single, it was necessary to compare corresponding parts of the lines of the exciting light and of the resonance light. This comparison was facilitated by the possibility of making several exposures on the same plate with the lines side by side.

The usual procedure was to first photograph the exciting light reflected from the magnesium oxide, then move the plate, turn the bulb and

expose to the resonance light, and at the end of the exposure again turn the bulb and move the plate and expose to the exciting light.

The exposures for the resonance spectrum varied from three to fifteen hours; usually twelve hours. The exposures for the diffusely reflected exciting light, to give the same intensity as the resonance light in 12 hours, were from fifteen to thirty minutes when the same type of flame was used. The brightest resonance is secured when the flame is quite faint. Wratten and Wainwright panchromatic plates were used.

The method of estimating the intensity ratio of the D lines, when both appeared, was to match the two lines with sodium lines on a comparison plate made by taking a series of exposures of varying length with a sodium flame of constant intensity. The intensity ratio was assumed equal to the ratio of exposure times of lines that matched.

RESULTS.

Most of the plates taken were of resonance excited by D_2, for as D_2 is about twice as bright as D_1, there are obvious advantages in trying it first. The efficiency of the polarization method of cutting out D_1 was tested and it was estimated that under the best conditions D_2 was at least 50 times as bright as D_1, though overlapping due to irradiation of the D_2 line made it impossible to be sure of the ratio.

The results of many exposures to resonance excited by D_2 showed visible traces of D_1 in nearly every case, but with an intensity ratio of D_2 to D_1 that varied from about 6 to 1, to about 20 to 1. This result led at first to the suspicion that stray sodium light was in some way thrown on the spectroscope slit. All possible precautions against this source of error were taken.

When with these precautions both D lines appeared in the resonance spectrum a further precaution was taken to be sure the effect was not false. A narrow horizontal strip of magnesium oxide was placed so as to intercept the rectangle of resonance light in such a way that part of the resulting spectrum line was formed by resonance, and part by reflected light. Since the resonance light is much fainter than the light reflected from a white surface the comparison strip was made a dark gray by first coating the bulb with smoke, and then depositing magnesium oxide until the reflected light was of about the same intensity as that of the resonance. Fig. 4 *A* shows the form of the oxide patch, the large rectangular strip being the same as that before mentioned, and the narrow shaded strip the part that intercepted the patch of resonance.

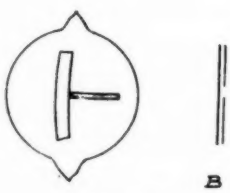

Fig. 4.

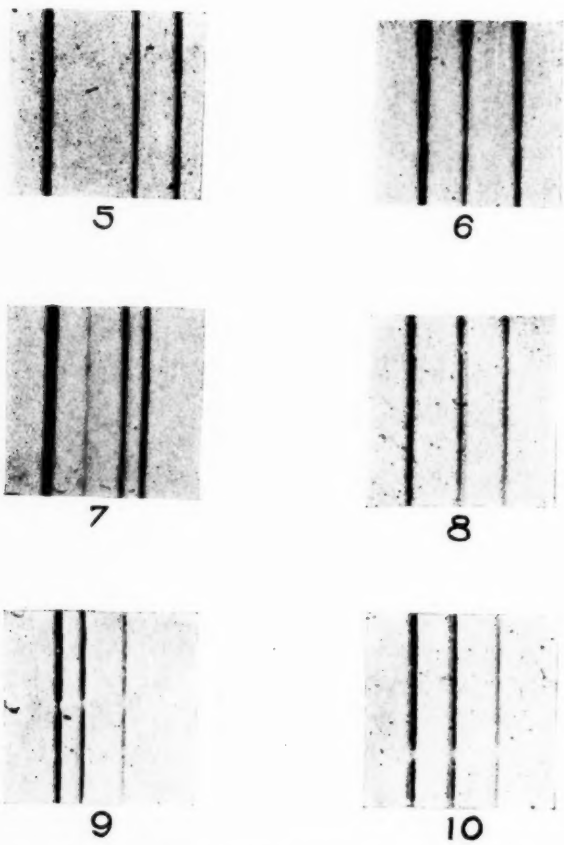

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Fig. 4 *B* shows the appearance of the resulting spectrum line as it appeared when this method was used. Both D lines appear except at the place where the exciting light is reflected from the gray strip into the spectroscope, and there only one line is recorded. If the appearance of both lines was due to reflection of stray light from the surface of the glass there would be no break in the line. This effect was found both with resonance excited by D_2 and by D_1, and seemed to be conclusive evidence that D_2 light did excite a trace of D_1 light in the resonance radiation. Having verified the results by this method the gray strip was dispensed with in the later work, as it somewhat complicated the adjustment of the bulb. On all plates, however, three exposures were taken, as is shown in the accompanying plate. The plates have been enlarged about ten times. In each case the middle line, or pair of lines, is the resonance spectrum, and the two lines on each side are due to the exciting light diffusely reflected from the patch of magnesium oxide. False effects due to any change in the exciting light can thus be detected.

Comparison of a number of plates taken under different conditions of temperature, with bulbs prepared in different ways, did not at first show clearly under what conditions D_1 appeared in the resonance spectrum excited by D_2. This was due to the fact that two causes contributed to the effect. However all the bulbs from which the hydrogen was not carefully removed showed D_1 distinctly. Now the resonance spectrum of iodine vapor excited by the green mercury line is changed in the presence of electro-positive gases such as helium and hydrogen, the effect of the gases being to transfer energy from the radiation centers directly excited by the mercury line to other radiation centers. The effect will be described later. The possibility of a similar effect in the case of sodium resonance led to the following experiments: The effect of a change in the density of pure sodium vapor on the resonance excited by D_2 was first investigated. A bulb containing sodium that was as free as possible from hydrogen was used for three exposures to resonance excited by D_2 at temperatures of 210°, 270° and 340° keeping all other conditions constant. The exposure at 210° showed no trace of D_1 in the resonance spectrum, while at 270° a distinct trace of D_1 was seen. At 340° the intensity ratio of D_2 to D_1 was about the same as that in a faint flame, about 2 to 1, but the plate was much under-exposed and the result therefore was subject to error. Figs. 5 and 6 of the accompanying plate show the resonance of pure sodium vapor excited by D_2 at 210° and 300° respectively.

It may be well to mention here the change in general appearance of the resonance as the temperature is raised. Resonance light becomes

visible at about 120°, and appears as a faint glow throughout the bulb. As the temperature is raised the light becomes brighter at the front surface and fades out in the interior of the bulb until, finally, the light is limited to the surface and exhibits a sharp image of the source when it is focused on the bulb. At 200° the resonance appears only at the surface though the image of the source is still a little indistinct, but above 250° the image is as sharp as if the light was reflected from a piece of smooth paper.

The change in the resonance spectrum when hydrogen was put into the bulb was more marked than the change when the vapor pressure of the sodium increased. The resonance excited by D_2 in a bulb containing .25 mm. of hydrogen showed D_1 about a quarter as bright as D_2 at 210° and at 300° D_1 was a third as bright as D_2. Figs. 7 and 8 were taken under these conditions. The faint line in Fig. 7 is of no importance.

A similar series of exposures was taken of the resonance excited by D_1. It is difficult in this case to avoid traces of D_2 in the exciting light for reasons before mentioned, and the intensity of the resonance is reduced to about half. The effect of increasing the vapor pressure or putting hydrogen in the bulb is the same in this case as with D_2 excitation, though the intensity ratio of D_2 to D_1 with D_1 excitation is greater than that of D_1 to D_2 with D_2 excitation when other conditions are the same. Thus with pure sodium at 210° a trace of D_2 was visible (Fig. 9) while with .1 mm. of hydrogen in the bulb D_2 is half as bright as D_1 (Fig. 10). Some plates, where more hydrogen was in the sodium bulb, showed D_2 nearly as bright as D_1 but the plates were underexposed and there was a possibility that the effect was false.

All the results mentioned above were verified by repetition of the experiments. In all about 50 plates were taken in which the resonance lines were distinct, and the other conditions favorable as far as could be ascertained.

Estimates of the intensity ratio of the D lines were made in each case. They agreed roughly under apparently similar conditions of vacuum, temperature of bulb, etc., but there was quite a range of uncertainty both in the estimation of the intensity ratio, and in the ability to get conditions identical in two cases. The observations may be summarized as follows:

D_2 EXCITATION.

Bulb as free from hydrogen as possible.

At 210° (no trace of D_1) intensity ratio of D_2 to D_1 at least 20 to 1. Fig. 5.

At 300°, ratio of D_2 to D_1 5 to 1. Fig. 6.

Bulb containing about .25 mm. of hydrogen.

At 220°, ratio of D_2 to D_1 4 to 1. Fig. 7.

At 300°, ratio of D_2 to D_1 3 to 1. Fig. 8.

D_1 EXCITATION.

Bulb free from hydrogen.

At 220°, a trace of D_2 seen. Fig. 5.

At 300°, ratio of D_1 to D_2 3 to 1.

Bulb containing .1 mm. of hydrogen.

At 220°, ratio of D_1 to D_2 2 to 1. Fig. 6.

Bulb containing .25 mm. of hydrogen.

At 250°, ratio of D_1 to D_2 possibly 3 to 2.

CONCLUSION.

As it has been shown that the presence of hydrogen causes both D lines to appear when resonance is excited by one D line only, it is safe to conclude that the appearance of both D lines at high temperatures is due to the increase of the pressure of the sodium vapor. From the measurements of vapor tension made by Hackspill[1] we can estimate the pressure of sodium vapor at the temperatures used. Extrapolating the vapor-tension temperature curve given by him gives the following values of vapor pressure:

At 200°, .003 mm.
At 250°, .01 mm.
At 300°, .025 mm.

Thus at 200° the vacuum is nearly as good as in a cold bulb, but at 300° the amount of sodium vapor is comparable to the amount of hydrogen present, in the bulbs made to show the effect of that gas.

There is a striking analogy to this effect of hydrogen and sodium vapor on the resonance spectrum of sodium, in the case of the resonance spectrum of iodine vapor excited by the green mercury line when traces of a chemically inert gas are present. This effect was described by one of us in 1911.[2] Iodine vapor at room temperature in a high vacuum when excited by the green line of the Cooper-Hewitt mercury arc emits a spectrum consisting of a series of doublets spaced at nearly equal frequency intervals. The first member is in coincidence with the exciting line and the last (or 28th) is at wave-length 7683. If a long exposure is

[1] Hackspill, Annales de Chemie et de Physique, 28, 680, 1913.

[2] Wood and J. Franck, Phil. Mag. (6), 21, p. 265.

given it is found that traces appear of very regular bands, similar in appearance to that of the A line of the solar spectrum. If helium at 3 mm. pressure is introduced into the bulb, the doublets weaken and the bands increase in intensity. As the helium pressure increases the doublets become fainter and the bands stronger in proportion; that is, there is a transfer of energy from the system or systems giving rise to the doublets, to that responsible for the band spectrum. The same thing occurs with xenon or krypton, or any other electro-positive gas. An electro-negative gas, however, merely decreases the intensity of the resonance, and so far as is now known, does not give rise to the transfer of energy. It is of course possible or even probable that there is some transfer in this case, but the intensity is so greatly reduced that its detection is difficult.

We conclude that the transfer of energy from the D_2 to the D_1 emission centers, or vice versa, is in some way the result of molecular collision, either of sodium with hydrogen or of sodium with sodium. It has been shown that hydrogen and sodium vapor, both electropositive, cause this transfer of energy, and the analogy to the similar transfer in the case of iodine resonance is of considerable interest.

In a bulb of pure sodium at 220° the surrounding vapor is not dense enough to have an observable effect on the radiation centers, and only one line appears in the resonance spectrum. The appearance of the other line results from an increase in the collision frequency, which increase can be caused either by the introduction of hydrogen at low pressure or by increasing the density of the sodium vapor.

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